EFFECTS OF MOISTURE ON WEAR OF COMPONENTS LUBRICATED WITH DIESEL FUEL

INTERIM REPORT
TFLRF No. 329

By
Paul I. Lacey
Jimell Erwin
U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI)
Southwest Research Institute
San Antonio, Texas

prepared for

Naval Surface Warfare Center
CARDEROCK Division
Shipboard Energy R&D Office
3A Leggett Circle
Annapolis, Maryland 21402-5067

March 1999

19990323 125

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instruction, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE March 1999	3. REPORT TYPE AND DATES COVERED Interim May 1996 – September 1997

4. TITLE AND SUBTITLE Effects of Moisture on Wear of Components Lubricated with Diesel Fuel	5. FUNDING NUMBERS DAAK70-92-C-0059; WD 24, 38
6. AUTHOR(S) Lacey, Paul I. and Erwin, Jimell.	

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI) Southwest Research Institute P.O. Drawer 28510 San Antonio, Texas 78228-0510	8. PERFORMING ORGANIZATION REPORT NUMBER TFLRF No. 329

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army TARDEC Petroleum and Water Business Area Warren, MI 48397-5000	10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
U. S. Army customer for this project is the Naval Surface Warfare Center, CARDEROCK Division, Code 859, Annapolis, MD 21402-5067

12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited	12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
The durability of some fuel injection systems on compression-ignition engines will be adversely affected by fuels of significantly low lubricity. Previous work has shown that fuel-lubricated wear is sensitive to the availability of moisture, particularly in severely refined fuels, which are designed to minimize exhaust emissions. The effects of moisture may be particularly relevant in a marine environment in which sea water is used as ballast in the fuel tanks. Traditional, less-refined fuels contain natural corrosion inhibitors that reduce oxidative wear, although alternate wear mechanisms may still affect long-term durability. However, no detailed study has been performed to define the effects of water contamination and its relationship to fuel composition. Standardized laboratory-scale tests that show good correlation with wear in full-scale fuel injection systems for ground vehicles are available. In the present work, the standard procedures for the HFRR and BOCLE/SLBOCLE apparatus were modified to show the effects of both dissolved and emulsified water on fuel-lubricated wear. The results indicate that the lubricity of all but the most severely hydrotreated fuels are insensitive to contamination by either deionized or salt water. Moreover, the relatively short aeration period used in the ASTM D 5001 and D 6078 BOCLE test procedures has no measurable effect on water concentration in the test fuel sample.

14. SUBJECT TERMS					15. NUMBER OF PAGES
Humidity	Boundary Lubrication	Bench Test	Corrosion Inhibitor	Diesel	27
Sea Water	Corrosive Wear	Water	Oxidative Wear	BOCLE	
HFRR	Contamination	Marine Diesel	F-76	Lubricity	16. PRICE CODE
Marine Fuel	SLBOCLE				

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

EXECUTIVE SUMMARY

Problems and Objectives: To meet emissions regulations, increasingly severe fuel refinery processes are being introduced that may remove the naturally occurring fuel components, which provide lubrication in the fuel injection system. A number of previous studies indicated that the wear mechanisms may also be sensitive to the availability of moisture. The objective of this present study is to better define the effects of moisture on wear of metal contact zones lubricated by fuels of varying quality.

Importance of Project: The fuel injection system is central to the reliable operation of compression ignition engines, which are prevalent throughout military service. The effects of moisture are expected to be particularly important for shipboard applications in which sea water is used to replace the fuel as ballast within the same tank.

Technical Approach: A number of standardized laboratory-scale wear tests are available to predict fuel lubricity. In the present study, these tests were modified to expose the test fuel to varying concentrations of water. Initial samples were exposed to dry and humid air, while other samples were exposed to bulk water. Finally, known volumes of either deionized or salt water were emulsified with the fuels. Each wear test procedure was performed with a range of fuel types that included good and bad lubricity, and high and low viscosity. The true water content of the hydrocarbon phase of the fuel samples was defined using a Karl Fischer automated titration, an Aquatest IV (or in some instances Accumet) apparatus.

Accomplishments: The results of the present study indicate that most fuels are normally saturated with dissolved moisture at ambient conditions. As a result, exposure to humid air and even bulk water has little effect on fuel-lubricated wear. The dissolved water is relatively difficult to remove from the fuel. As a result, the brief aeration process used on the BOCLE wear tests described in ASTM D 5001 and ASTM D 6078 have little effect on either water concentration or wear. It also appears that the mathematical correction that accounts for the effects of humidity, as defined in both the ISO/DIS 12156-1.3 and CEC F-06-A-96 procedures for the HFRR, are not accurate when applied to the fuels evaluated in this study.

Military Impact: The Naval Surface Warfare Center is currently planning a program to define the effects of refining severity on the lubricity of F-76 marine diesel fuel. The study will evaluate the effects of hydrotreatment and composition on fuel-lubricated wear. The results of this report indicate that the effects of neither fuel moisture content nor exposure to salt water need be evaluated in detail in the planned test matrix.

FOREWARD/ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

I.   OBJECTIVE

The objective of this study is to define the effects of humidity, deionized water, and salt water on the lubricity of diesel fuels, with particular reference to F-76 marine diesel.

II.   BACKGROUND

Currently, both military and commercial diesel fuel specifications are being revised.(1)* This process may result in the production of more severely refined fuels that are devoid of the traditionally naturally occurring, reactive components necessary for effective lubrication and wear prevention. Indeed, high injection-system failure rates, due to the commercial sale of very highly refined low-sulfur diesel fuels, have been reported in Scandinavia. The situation in Scandinavia and in military equipment has been controlled through the empirical inclusion of lubricity additives in the fuel. However, no specification for minimum acceptable protection, due to variation in additive quality or concentration, is available.

The present report forms part of a larger effort sponsored by the Naval Surface Warfare Center, CARDEROCK Division (NSWCCD) to define the effects of increasingly severe hydrotreatment on the expected wear resistance of NATO F-76 (MIL-F-16884J) diesel fuels.(2) The approach planned for the Navy study is to use laboratory scale wear tests to evaluate successive levels of hydrotreatment in a range of commercially available fuels. However, effective laboratory wear test simulation of a real environment requires accurate reproduction of the principal wear mechanisms present.(3) In particular, Navy ships commonly use sea water as ballast to replace the weight and volume of fuel withdrawn from storage tanks. As a result, the potential effects of direct contact with salt water on the fuel's lubricating characteristics must be considered.

Previous publications (4-6) have described the development and application of a wear-mapping technique using the Cameron-Plint apparatus, which provides a range of lubricated contact conditions appropriate to injection systems. This technique delineated the principal wear mechanisms likely to exist at the conditions present in various segments of the fuel injection

---

* Underscored numbers in parentheses refer to the list of references at the end of this report.

system. At lower loads, material removal with fuels devoid of natural or artificial corrosion inhibitors was primarily described by an oxidative wear mechanism. Regulation of either moisture or oxygen availability affected wear rate under these conditions. However, the weak boundary and surface oxide films were easily removed, resulting in intermetallic adhesion and severe scuffing at slightly higher loads. Typical boundary lubricants, which are effective at low loads, consist of oxygenates, among which are those materials based on dilinoleic acid specifically approved as corrosion inhibitor additives in MIL-I-25017.(14) In contrast, low concentrations of corrosion inhibitor additives have little effect on adhesive wear resistance and scuffing load capacity. As a result, an imperfect correlation was found to exist between the wear rate under lightly loaded conditions and adhesive wear resistance.

The objective of the work described in this report is to define the importance of moisture in fuel-lubricated wear, using well-accepted laboratory-scale test procedures. The test conditions produced by the different laboratory procedures simulate each of the principal wear mechanisms believed to exist in injection systems. If the effects of salt water were found to be significant, a new procedure unique to the Navy may be required and would be used in the remainder of the Navy study.

III. APPROACH

A.   DESCRIPTION OF WEAR TEST APPARATUS

Ball on Cylinder Lubricity Evaluator: Laboratory-scale wear tests were performed using the Ball-on-Cylinder Lubricity Evaluator (BOCLE) shown in Figures 1 and A-2[1]. The machine is an InterAv model, No. BOC-100-007. In this apparatus, a 0.5-inch diameter AISI E 52100 steel ball is pressed against a rotating cylinder made of SAE 8720 steel. The lower half of the cylinder is immersed in a fuel bath and carries fuel to the contact area. The BOCLE may be operated using two different test procedures: ASTM D 5001 and ASTM D 6078, as described in Table 1.

---

[1] If figure and table numbers include a letter, the letter is the appendix reference and the number is the chronological reference within the appendix, e.g. A-2 is Figure 2 in Appendix A.

2
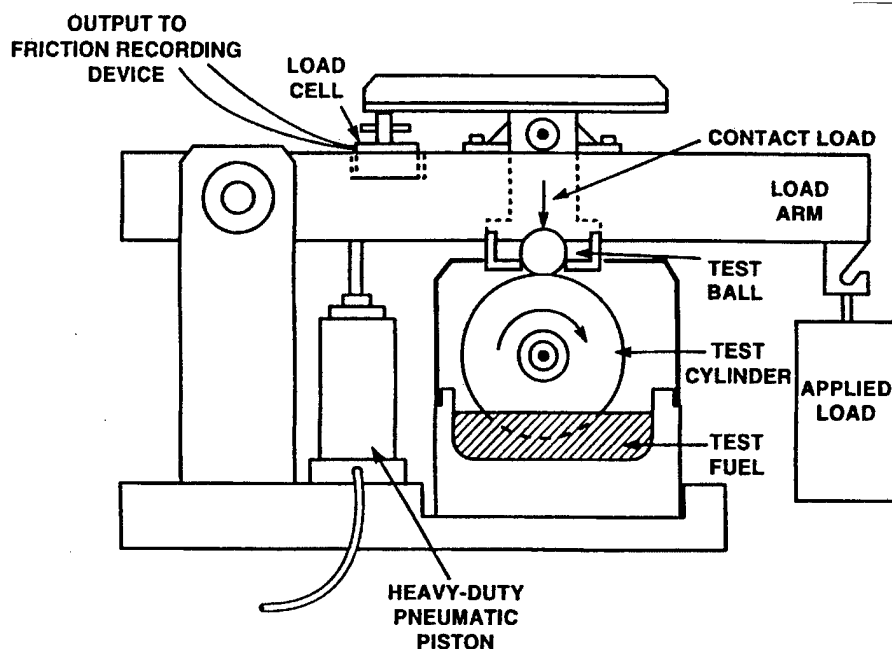
Figure 1. Schematic Diagram of the Ball-on-Cylinder Lubricity Evaluator (BOCLE)

TABLE 1. Operating Conditions for the Laboratory Scale Wear Tests

Test Parameter	SLBOCLE (ASTM D 6078)	BOCLE (ASTM D 5001)	HFRR (ASTM D 6079)
Applied Load, kg	1 to 5 (variable)***	0.5***	0.2
Speed	525 RPM	240 RPM	50 Hz
Break-in, sec/kg	30/0.5	None	None
Duration, min	1.0	30	75
Atmosphere	Controlled Air	Controlled Air	Uncontrolled**
Humidity, %RH	50**	10**	Ambient**
Fluid Temp., °C	25	25	25
Pass/Fail****	3 kg min	0.65 mm max	0.36mm max
Stroke Length,mm	–	–	1

* For tests performed at 25°C
**The relative humidity values provided are those used in the standard test procedures. Non standard tests at other humidity conditions were used in the present study, as described in the text.
***The true contact load is twice the applied load.
**** These pass/fail limits reflect those typically used in industry.

The ASTM D 5001 procedure is a single-load, mild wear test, which is primarily sensitive to oxidative/corrosive wear. The wear volume formed on a 0.5-inch diameter ball is taken as a measure of lubricity for each fuel. The complete procedure, including pretest cleaning of the specimens, is defined in Reference 7. The wear test is performed at a sliding speed of 240 rpm and an applied load of 500 grams (equivalent to a contact load of 1000 grams) over a duration of 30

minutes. In the standard procedure, the relative humidity of the air above the fuel reservoir is closely controlled at 10 percent. A 15-minute aeration period is used prior to each test, during which 0.5 L/min of air is bubbled through the fuel and 3.3 L/min is passed over the fuel. During the 30-minute test, 3.8 L/min of controlled humidity air is passed over the fuel. Following the test, the wear scar diameter on the ball is measured using an optical microscope, and the result is reported as the mean diameter of the elliptical wear scar formed, where mean diameter is (A+B)/2.

The Scuffing Load Ball On Cylinder Lubricity Evaluator (SLBOCLE) is a measure of the fuel's ability to lubricate under conditions of high contact stress, which result in severe scuffing. The procedure may be obtained in ASTM D 6078. This is a relatively new technique, which has not yet been printed by ASTM, so a complete copy is provided in Appendix B. The ASTM D 6078 test consists of a series of incremental loads to define the applied load required to initiate severe adhesive wear or scuffing. The test specimens and contact parameters were selected to provide a very distinct transition between mild and severe wear. The test apparatus was modified to allow measurement of friction coefficient to better define the wear transition. Each load increment is performed over a one-minute period at a sliding speed of 525 rpm. In the ASTM D 6078 standard test procedure, the relative humidity of the air above the fuel reservoir is controlled at 50 percent, while the air-flow rates are identical to those used in the ASTM D 5001 procedure. The final result is reported as the average applied load in grams required to cause adhesive scuffing, as defined using two separate test specimens.

High Frequency Reciprocating Rig: The HFRR apparatus is a measure of the fuel's ability to resist adhesive wear produced under relatively high contact stress. A schematic diagram of the HFRR apparatus is shown in Figure 2, and a photograph is provided in Figure A-1. In the standard ASTM D 6079 procedure, the fluid is placed in the reservoir of the rig and the temperature maintained at 25°C. Alternate procedures are available at 60°C. However, these were not used in the present study due to the possibility of evaporating lighter fuel fractions. During testing, a fixed steel ball is held in a vertically mounted chuck and forced against a horizontally mounted stationary steel plate with an applied load. The test ball is oscillated for 75 minutes and fully immersed in the fluid reservoir. The stroke length, temperature, load, and frequency are specified in Table 1. The final procedure for the HFRR is not yet available in print from ASTM. The methodology used in

4

the present study is provided in Appendix C. No attempt is made to control humidity in the standard ASTM D 6079 procedure for the HFRR apparatus. The wear scar generated on the test ball at the conclusion of the test is a measure of the fluid's lubricating properties. The HFRR apparatus also provides a record of the electrical contact resistance between the upper and lower specimens during the relative motion. The value of the contact resistance reflects the strength of the boundary lubricating film formed between the surfaces.
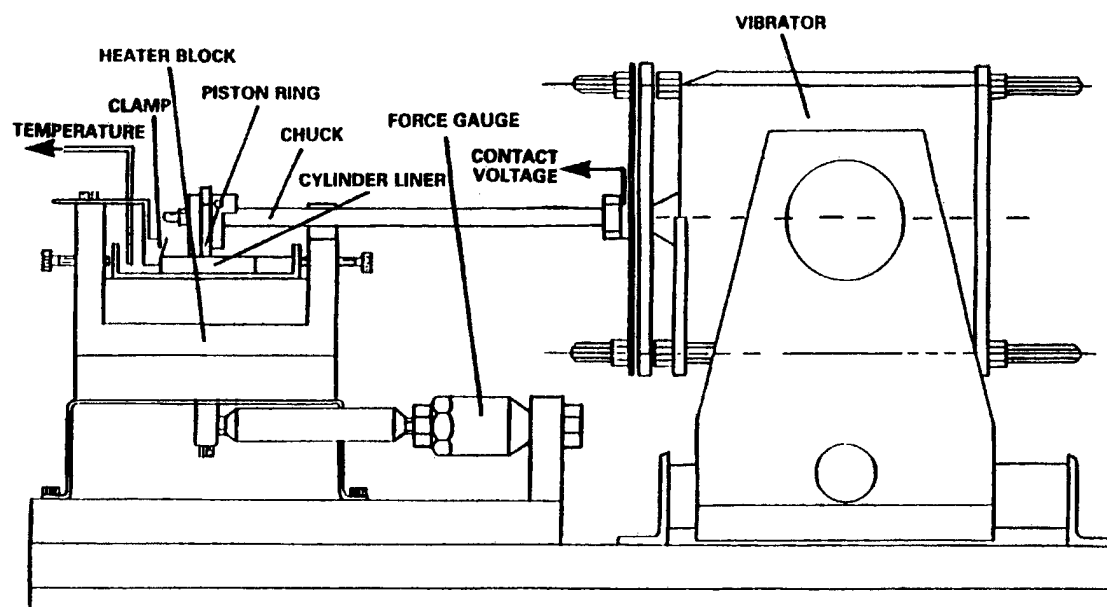
Figure 2. Schematic Diagram of the High Frequency Reciprocating Rig (HFRR)

B.   TEST FUELS

Fuel Characteristics: Laboratory scale wear tests were performed using the six fuels described in Table 2. These fuels were selected to cover a wide range of chemical characteristics and associated lubricities. In addition, none of the base fuels were expected to contain additives specifically intended to affect lubricating characteristics. The sulfur content of each fuel sample was measured using ASTM D 4294, while the aromatics content was measured using ASTM D 5186. Both the Jet A-1 and Isopar-M fuels are very clean low-sulfur fuels, and therefore expected to be highly sensitive to the effects of moisture contamination. The Jet A-1 fuel was also tested with 20 mg/L of DCI-4A corrosion inhibitor additive. For the purposes of lubricity, this blend is effectively equivalent to JP-8 without the anti-static and anti-icing additives. The Reference No 2

5

fuel, commonly referred to as Cat 1-H, is an example of a good lubricity, high-sulfur diesel fuel. The Gold Line fuel is an example of a naturally low-sulfur F-76 marine diesel with good lubricity. Finally, the California diesel is an example of a low-sulfur, low-aromatic-content fuel, as currently sold in the San Francisco area and meets the requirements of the California Air Resources Board. This particular California diesel fuel has medium to poor lubricity.

TABLE 2. Characteristics of Test Fuels

Fuel Type	Laboratory Reference	Sulfur[†] wt%	Viscosity cSt @ 40C	Aromatics[*], Mass %		
				Total	Di	Poly
Reference No. 2	AL-20573-F	0.42	3.02	27.8	10.5	1.3
Jet A-1	AL-20844-F	<0.01	1.07	11.0	0.8	0.1
Jet A-1 + DCI 4A	Blend	<0.02	1.07	11.0	0.8	0.1
ISOPAR-M	AL-20239-F	0.0	2.79	0.0	0.0	0.0
California Fuel	AL-23985-F	<0.01	3.84	<2	0.49	0.1
Gold Line	AL-24254-F	0.06	3.47	16.9	4.7	1.1

[*]Aromatic concentration was defined using supercritical fluid chromatography per ASTM D 5186
[†]Sulfur content was defined using ASTM D 4294

Synthetic Sea Water: A number of wear tests were performed to define the potential effect of salt water contamination on fuel lubricity. The fuel samples were blended with synthetically manufactured salt water, produced as described in ASTM D 665. The composition of the synthetic sea water is provided in Table 3. A five-gallon batch was blended using water deionized prior to the study and stored in a cool box in a new, clean, plastic container. Samples were taken directly from the container and blended with the appropriate fuel on an as-needed basis.

TABLE 3. Composition of Synthetic Sea water as Described in ASTM D 665

$NaCl$	24.54
$MgCl_2 \cdot 6H_2O$	11.10
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.69
$NaHCO_3$	0.20
KBr	0.10
H_3BO_3	0.03
$SrCl_2 \cdot 6H_2O$	0.04
NaF	0.003

C.   CONTROL OF FUEL WATER CONTENT

Measurement of Fuel Moisture Content: The water content in the majority of fuel samples was measured using an Aquatest IV instrument, as manufactured by Photovolt Corporation and shown in Figure A-3. The Aquatest IV is more accurate than manual titration procedures, e.g., ASTM D 1744, which it has largely replaced. The Aquatest IV apparatus is capable of evaluating water concentrations from approximately 10 PPM to 100 percent. A complete description of the Aquatest IV is provided in Appendix D. Due to mechanical failure of the Aquatest IV apparatus, a number of samples were evaluated using the Accumet apparatus described in Appendix E. This apparatus was only used to evaluate the samples detailed in Tables F-7 and F-8. Both instruments implement the same titration chemistry.

The Aquatest IV and Accumet apparatus were calibrated at 0, 100, and 25,000 PPM water. The correlation between the Aquatest IV and the Accumet was also defined using identical samples of Reference No. 2 and Jet A-1 fuels, with the results in Table 4. Good correlation was observed between the two test apparatus during duplicate tests with the Reference No. 2 fuel. For Jet A-1, the Aquatest IV consistently gave a result approximately 25 PPM lower than the Accumet. Given the good correlation for Reference No. 2 fuel, the cause of this discrepancy with Jet A-1 was not apparent.

TABLE 4. Comparison of Fuel Water Content Results Obtained Using
Aquatest IV and Accument Apparatus

Water content, PPM

Run #	Reference No. 2		Jet A-1	
	Aquatest	Accumet	Aquatest	Accumet
A	98	94.5	42	68.8
B	99	93.2	41	68.7

For each fuel/water concentration, the ASTM D 6078 and ASTM D 5001 BOCLE tests were performed sequentially using the same 50 mL fuel sample. As a result, three fuel samples were drawn directly from the BOCLE test reservoir for evaluation using the Aquatest IV apparatus. Samples were taken immediately before and after the ASTM D 6078 SLBOCLE test (Note: the pretest sample was taken following aeration). The third sample was taken immediately following completion of the ASTM D 5001 BOCLE test. The HFRR apparatus used a small sample volume

7

of 2 mL. Different sampling procedures were used for the fuel samples from the HFRR apparatus depending on the test procedure used, as will be described in the following sections. Prior to evaluation using the Aquatest IV or Accumet apparatus, the fuel samples were stored in sealed 20 mL containers, which were rinsed with acetone to eliminate residual moisture. All moisture determinations using the Aquatest IV and the Accumet were performed in duplicate.

Control of Moisture Content Using Ambient Humidity: The laboratory-scale wear tests for the BOCLE described in ASTM D 5001 (7) and ASTM D 6078 (8) (Appendix B) attempt to standardize fuel moisture content by control of ambient humidity around the reservoir. During these tests, the relative humidity of air passed through and over the test fuel is regulated to 10 and 50 percent, respectively. In contrast, no attempt was made to routinely regulate the moisture content of fuel tested with the HFRR procedure described in ASTM D 6079 and contained in Appendix B. (9) However, the CEC F-06-A-96 procedure for the HFRR apparatus (15) requires that the ambient humidity of the test laboratory be within a certain range and that a humidity correction factor be used. In the present study, BOCLE and HFRR tests were performed using fuel samples aerated at 0, 10, 50 and 100 percent relative humidity. The air was bubbled through the fuel and blown over the fuel for 15 minutes prior to each test. This aeration through and over the fuel continued throughout the duration of each test.

The existing fuel aeration system design was found to be satisfactory for both of the BOCLE tests. However, the relatively small fuel volume used in the HFRR apparatus precludes direct aeration of the two-mL fuel sample. Instead, the fuel was preaerated outside the wear test chamber using the apparatus shown in Figure A-1. Air with controlled humidity was provided from the BOCLE apparatus at a flow rate of 3.8 L/min and sparged through the fuel in the preaeration chamber. The fuel samples for evaluation of moisture content were taken directly from the preaeration chamber. During each wear test, the aerated fuel was delivered to the HFRR reservoir at a flow rate of 1 mL/min for a total fuel volume of 77 mL. The aeration of the fuel in the chamber continued throughout each test. However, by periodic additions, a constant fuel volume was maintained in the preaeration chamber throughout the 75-minute test. A fitted cover was manufactured for the HFRR reservoir to prevent atmospheric contamination of the fuel sample during its residence period in the HFRR. The standard HFRR reservoir was modified to provide an outlet for any

8

excess fuel, which was not recycled. During each 75-minute HFRR test, air with the appropriate humidity level was passed over the fuel to ensure that water concentration remains constant. Other than control of humidity, both the BOCLE and HFRR tests were performed at the standard conditions detailed in Table 1.

Extended Aeration to Control Moisture Content: A number of tests were performed to define the effects of extended aeration on fuel moisture content and wear. These tests were performed using fuel that had been predried as described later in Section C of this report. The dry fuel was aerated for 48 hours in the stainless steel BOCLE reservoir at the conditions defined in ASTM D 5001. The complete 48-hour aeration process was performed at 0, 10 and 100 percent humidity, at the conditions defined in Table 6. The air was bubbled through and over the fuel during the complete 48-hour cycle. Laboratory-scale wear tests were performed according to the BOCLE, SLBOCLE and HFRR procedures after 0.5 and 48 hours of aeration. The 2-CC sample for the HFRR test was removed from the BOCLE reservoir. A separate measurement of water concentration was not performed on the HFRR test sample, because it can be assumed to be equal to that of the BOCLE from which it was removed. Air with the appropriate humidity was blown over the sample in the HFRR apparatus throughout the 75-minute test.

Control of Moisture Content by Exposure to Bulk Water During Testing: Bulk samples of 1.00 and 0.04 mL of either deionized or salt water were placed at the bottom of the BOCLE and HFRR fuel reservoirs, respectively. This corresponds to a fuel water ratio of 2.0 percent in each instance. No further attempt was made to blend the fuel and water. The bulk water sample remained in the reservoirs for the 15-minute pretest aeration in the BOCLE and also during the complete wear test in both the BOCLE and HFRR. Air was not bubbled through the fuel during testing to prevent forced mixing of the fuel and water. However, air with a relative humidity of 100 percent, was passed over the fuel at the standard flow rate during both the HFRR and BOCLE tests to prevent evaporation of moisture. The remaining test conditions were identical to those described in Table 1. The samples for evaluation of moisture content using the Aquatest IV apparatus were taken directly from the BOCLE fuel reservoir, being careful not to remove the bulk water. Approximately 1.5 mL of fuel was removed directly from the reservoir of the HFRR apparatus

9

following conclusion of each test, leaving 0.04 mL of water and 0.5 mL of residual fuel in the reservoir.

Control of Moisture Content by Presoaking with Bulk Water: To define the effects of larger water concentrations blended over an extended time period, 100 mL of fuel was placed in a closed container with an equal volume of either deionized or salt water. The container with the fuel and water was thoroughly shaken for 30 seconds and allowed to separate for 18 +/–1 hours. Immediately prior to testing, the required fuel volume was carefully removed, leaving the bulk water behind in the container. A photograph of the container in which the mixing was performed is provided in Figure A-6. HFRR and BOCLE wear tests were performed with fuel samples removed from the container according to the standard conditions detailed in Table 1. Fuel aeration was not performed prior to the BOCLE test (air passed through and over the fuel). However, moist air with a relative humidity of 100 percent, was passed over the fuel (but not bubbled through the fuel) during both the BOCLE and HFRR tests to prevent loss of moisture. The fuel samples for evaluation of moisture content using the Aquatest IV were taken directly from the reservoir of the wear test apparatus in each instance.

Control of Moisture Content by Emulsification with Water: Five and 10 vol% of both deionized and salt water were emulsified with the fuels using a 100-watt Vibracell ultrasonic mixer manufactured by Sonics and Materials Inc., Danbury, CT. For the BOCLE, the fuel/water blends were emulsified in the 50-CC reservoir for 30 seconds immediately prior to performing the ASTM D 6078 SLBOCLE test. The emulsifier was switched off during the relatively short ASTM D 6078 tests, but was operated continuously during the subsequent ASTM D 5001 BOCLE tests, which were performed with the same fuel sample. For the HFRR test, a 50-mL fuel sample was emulsified for one minute with an appropriate volume of water in a glass beaker. A series of photographs showing emulsification of a sample to be used in the HFRR are provided in Figures A-4A – A-4C. Following emulsification, a 2-mL sample was placed in the fuel reservoir, and the HFRR test started immediately. Every five minutes, the fuel/water mixture was emulsified for 30 seconds in the beaker and a fresh 2-mL sample placed in the HFRR reservoir using a syringe. The previous fuel sample was allowed to drain from the reservoir through an overflow to a glass beaker and was not recirculated.

10

No preaeration of the sample was performed to minimize separation of the fuel/water emulsion. However, moist air with a relative humidity of 100 percent, was passed over the fuel (but not bubbled through the fuel) during the BOCLE and HFRR tests to minimize loss of moisture. The remaining test conditions for the BOCLE and HFRR apparatus are identical to those described in Table 1. In each instance, the fuel samples for evaluation using the Aquatest IV apparatus were taken immediately following the ultrasonic mixing process. The Aquatest IV measurement includes all forms of water in the sample placed in the instrument, both dissolved water in the hydrocarbon phase and any entrained (emulsified) water. The BOCLE samples were taken directly from the fuel reservoir, while the HFRR samples were taken from the mixing beaker.

Fuel Predrying to Remove Dissolved Water: A limited number of tests were performed using Reference No. 2 and Jet A-1 fuels that had been dried to remove dissolved water. The objective was to remove the water present, while leaving the minor, polar components, believed to govern boundary lubrication, undisturbed. The Reference No. 2 fuel was dried by distillation, while the Jet A-1 was dried using a column of attapulgus clay. As previously stated, the severely hydrotreated Jet A-1 is used as a standard low-lubricity fuel at SwRI. As such, it is occasionally clay treated to remove water and any degradation products that may have formed during storage and contains few surface active compounds. The dry fuel was stored in epoxy-lined metal containers with a delivery tube installed so that the dry liquid could be placed directly in the lubricity tester without air contact.

To dry the Jet A-1, a clean, dry, glass column 45 mm in diameter by one meter long, was set up on a ring stand. One liter of Attapulgus clay was dried in an oven at 205°C for three hours. After drying, the clay was poured into the column to a depth of 40 cm and immediately sealed with a rubber stopper. A glass funnel was set up with a dried #41 Whatman filter at the tip of the column to remove any particles of clay that might pass through the glass frit at the bottom of the column. The end of the glass funnel was placed into the quart can along with a quarter-inch tube connected to a nitrogen bottle. Nitrogen was then flowed through the system to remove any existing air or moisture. The Jet A-1 sample was poured onto the column and percolated through

the clay until 25 mL had passed through the filter. This initial material was discarded, and the remaining sample was filtered directly into the quart can. The can was filled with nitrogen prior to delivery of the fuel and was constantly purged with nitrogen during filling. The nitrogen delivery tube reached the bottom of the container, and delivery continued until the container was sealed.

Clay treatment would affect the lubricity characteristics of the high-sulfur Reference No. 2 fuel. Instead, 800 mL of Reference No. 2 fuel was distilled under vacuum with a flow of dry nitrogen through the liquid. A total of 5V% was distilled overhead into the predried receiver, and under vacuum. No "ring" of water was observed as the first liquid was distilled over as might be seen in a particularly wet sample. No water was found in the receiver. However, there was a water phase in the cold trap in the vacuum line of about 0.5 mL with twice as much light hydrocarbon. Both the overhead and the bottoms samples were handled inside a glove bag purged with dry nitrogen and placed into epoxy-lined metal cans fitted with siphon tubes in rubber stoppers. The overhead and bottoms from the distillation were checked for water content. Overhead was 53 PPM, while the bottoms showed 32 PPM. The bottoms water content was higher than expected, since the distilling flask was heated to 193°F under vacuum at 3.8 mmHg.

A number of approaches were evaluated in an attempt to further reduce the water content of the Reference No. 2 fuel. The bottoms samples were shaken with dried sodium sulfate, calcium carbonate, calcium oxide, silica gel, phosphorous pentoxide, and sodium metal chips. The measured water concentration in each is provided in Table 5. The first two agents hold water by hydration, a very weak interaction, but usually effective on wetter samples. The remainder of the desiccants form a chemical bond with water of varying degrees of strength. Silica gel's bond is readily reversible, but the others form stronger bonds that give up water only by supplying enough energy to break the newly formed bond. However, each of these approaches may alter the composition of the test fuel and its associated lubricity. As a result, only the untreated bottoms sample was selected for lubricity testing.

12

TABLE 5. Effect of Desiccants on Water Content of Reference No. 2 Diesel

Desiccant	Water, PPM
sodium sulfate	60
calcium carbonate	43
silica gel	58
calcium oxide	52
phosphorous pentoxide	90
sodium metal chips, 4 Hrs	30
sodium metal chips, 4 Days	13

IV. RESULTS

A. Data Format

The test matrix used to define the effects of moisture on fuel-lubricated wear is summarized in Table 6. The standard conditions for each wear test procedure are highlighted in bold print. Except as discussed in the footnote to Table 6, the complete matrix was performed with each of the six fuels defined in Table 2. The results obtained are provided in Appendix F and plotted in Figures 3, 4, and 5. In each figure, two graphs share the same X axes. Each position on the X axes represents a different approach to introducing water to the test fuel, generally becoming more severe from left to right. The left side of each figure corresponds to tests performed with no bulk water present in which moisture content is controlled by ambient humidity only. The data towards the middle of each figure was produced with either 2-percent bulk water at the bottom of the fuel reservoir or presoaking equal volumes of fuel and water overnight. Finally, the data toward the right side of each figure were produced from fuel that was emulsified with water immediately prior to, and/or during, the wear test.

The upper graphs in each of Figures 3, 4, and 5 show data obtained using the respective wear test procedures at each of the different moisture conditions using the HFRR and BOCLE procedures, respectively. In each instance, the plotted data is the average of duplicate wear tests at each condition with each fuel. The lower graphs show the fuel moisture content in parts per million (Vol% for the emulsified samples) at the identical water pretreatment conditions.

13

TABLE 6. Test Matrix to Evaluate Effects of Moisture*

Test Designation	Duration of Pretreatment	Pre-Test Air Flo Thru/Over Fuel (L/min)	Rel. Humidity (%)	D 5001	D 6078	D 6079
Baseline HFRR	None	None	None	--	--	X
Humid Air						
Std. Aeration	15	0.5/3.3	0	X	X	X
Std. Aeration	15	0.5/3.3	10	X†	X	X
Std. Aeration	15	0.5/3.3	50	X	X‡	X
Std. Aeration	15	0.5/3.3	100	X	X	X
Extended Aeration**	48 hrs	0.5/3.3	0	X	X	X
Extended Aeration**	48 hrs	0.5/3.3	10	X	X	X
Extended Aeration**	48 hrs	0.5/3.3	100	X	X	X
Water in Reservoir						
Deionized water	15 mins	0/3.8	100	X	X	X
Salt water	15 mins	0/3.8	100	X	X	X
Pre-Soak						
Deionized water	None	None	100	X	X	X
Salt water	None	None	100	X	X	X
Emulsified Water						
Neat fuel	None	None	100	X	X	X
Deionized water (5 %)	None	None	100	X	X	X
Salt water (5 %)	None	None	100	X	X	X
Deionized water(10%)	None	None	100	X	X	X
Salt water (10 %)	None	None	100	X	X	X

*All conditions and procedures other than those listed in this table are in accordance with the respective standard methods. All tests are run in duplicate with each of the six fuels defined in Table 2.
** Extended aeration tests performed with Reference No. 2 diesel fuel and Jet A-1 only
†Standard method conditions of ASTM D 5001.
‡Standard method conditions of ASTM D 6078.
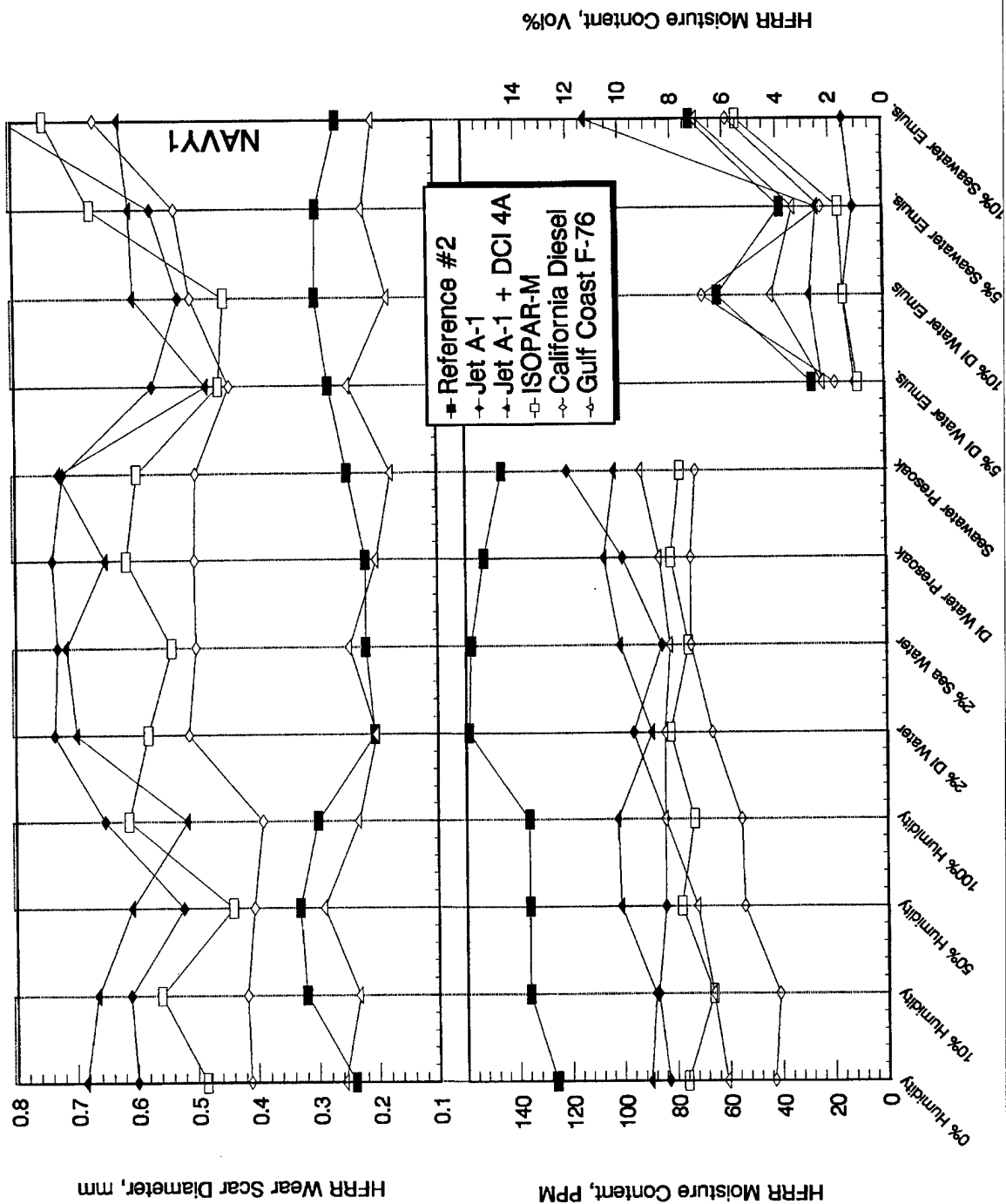
Figure 3. Summary of Averaged Wear Test Data Obtained Using the High Frequency Reciprocating Rig (HFRR) According to a Modified Version of ASTM D 6079

15
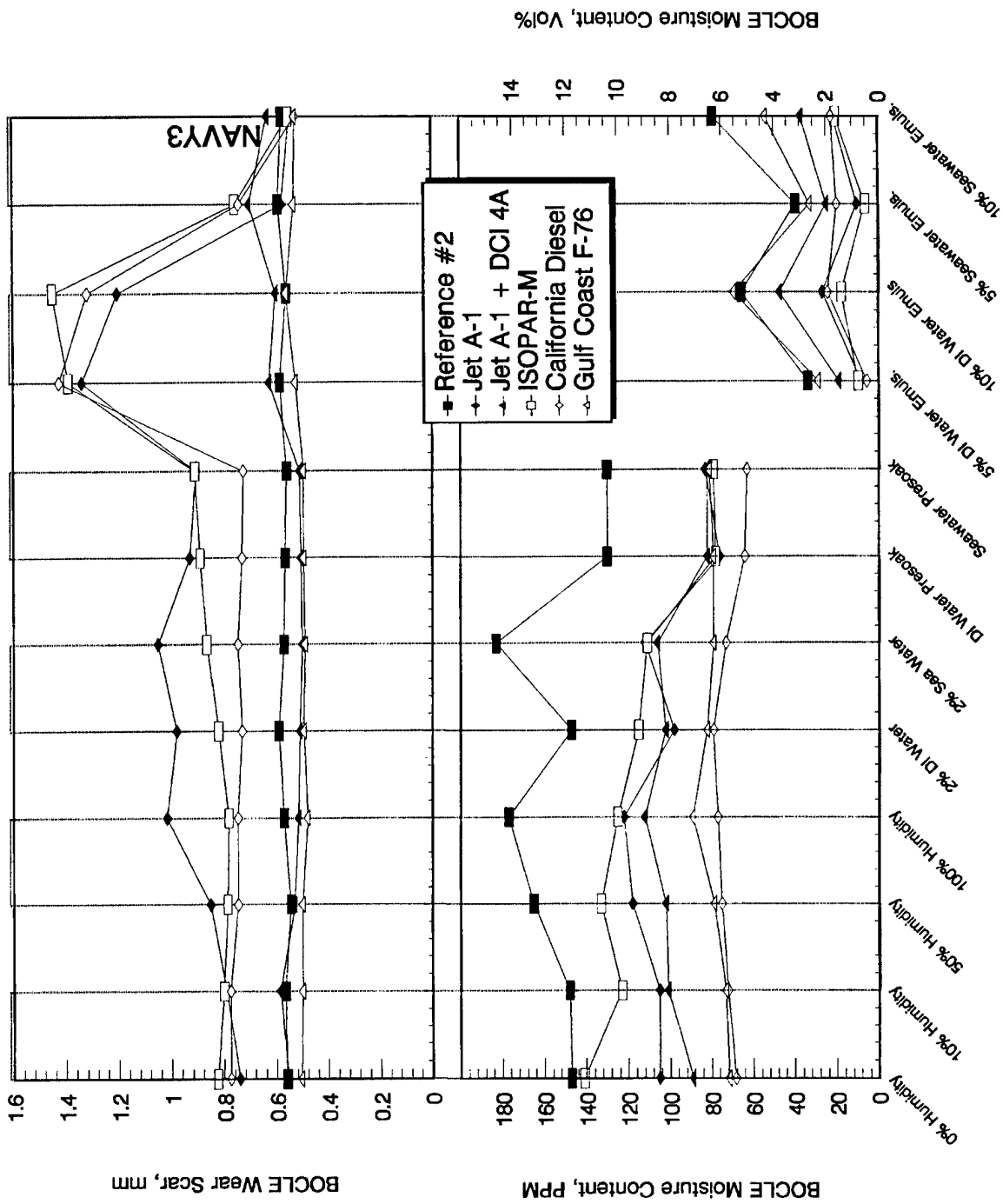
Figure 4. Summary of Averaged Wear Data Obtained in BOCLE Tests Performed According to a Modified Version of ASTM D 5001

16
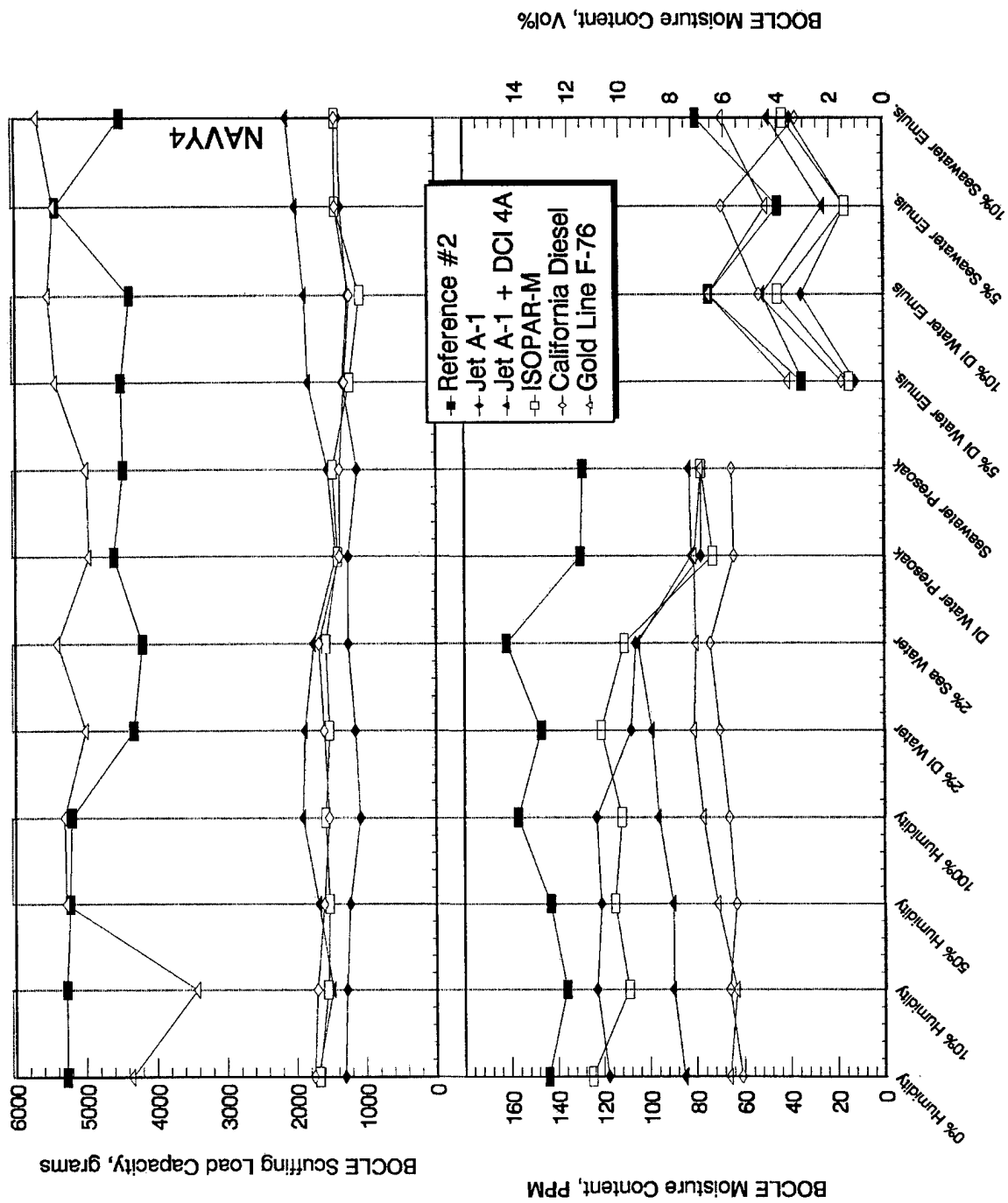
Figure 5. Summary of Averaged Wear Data Obtained in SLBOCLE Tests Performed According to a Modified Version of ASTM D 6078

17

B.   Fuel Moisture Content Results

The moisture content of each fuel from the duplicate HFRR tests, as measured using the Aquatest IV apparatus, are provided in Table F-2. For most of the duplicate wear tests, the moisture content in the test fuel was again performed in duplicate. The duplicate tests were performed with samples taken immediately before and after the 75-minute test. As a result, the fuel moisture content plotted in Figure 3 for the HFRR is the average value obtained from four Aquatest IV runs. The ASTM D 6078 SLBOCLE and D 5001 BOCLE tests were performed sequentially using the same fuel sample. As a result, the moisture content of the fuel used in both BOCLE procedures is contained in Table F-6. Three sets of fuel moisture content results are provided for each set of fuel pretreatment conditions. These correspond to the pretest, between test, and post test fuel samples in the BOCLE. The pretest sample was taken following aeration. Since each Aquatest IV analysis was performed in duplicate, the water concentration data points plotted in Figures 4 and 5 are the average value obtained from numerous individual Aquatest measurements. The moisture content data in Figures 4 and 5 are not identical. The SLBOCLE data in Figure 5 is the average of the pre- and mid-test data, while the BOCLE data in Figure 4 is the average of the mid- and post-test data.

Similar trends were observed between the water concentration in fuels sampled from the HFRR and both BOCLE tests. Significant differences exist between the ability of each fuel to hold water. In general, the Reference No. 2 fuel had approximately twice the water content of the California and Gold-Line diesel fuels, with Jet A-1 and ISOPAR-M having an intermediate value. The relatively low concentration (20 mg/L) of DCI-4A corrosion inhibitor additive appeared to have no effect on water solubility in Jet A-1. However, a higher additive concentration would likely have increased the propensity of the fuel to carry water. The different water treatment processes had surprisingly little effect on the concentration of dissolved moisture in the test fuel. Typically, an increase in water concentration was observed as ambient humidity was increased from 0 to 100 percent. However, exposure to bulk water (except for emulsified fuel/water) had little or no additional effect on water concentration. Indeed, presoaking with water appeared to reduce the water content of the test fuel in some instances, possibly due to removal of polar compounds by the bulk water.

Significant amounts of water were contained in the emulsified fuel, although the measured volume was always somewhat lower than what water was originally added. The ability of each fuel to

18

maintain a fuel water emulsion was not directly related to its ability to contain dissolved water. In every instance, Cat 1-H contains more water than the other fuels. However, the Gold Line and California fuels, which contained little dissolved water, carried appreciable amounts of emulsified water. This anomaly is probably due to the different relative importance of the chemical and physical characteristics, which are required to hold dissolved and emulsified water.

C.   Wear Test Results

Significant differences exist between the measured lubricities of the six neat test fuels. The Cat 1-H and Gold Line fuels show the best lubricity, with Jet A-1 and ISOPAR-M having the worst. The addition of 20 mg/L DCI 4A lubricity additive to Jet A-1 had a very slight beneficial effect on SLBOCLE scuffing load capacity, and no consistent effect on the HFRR result. In contrast, a very distinct improvement in lubricity was produced by the DCI 4A additive as measured by the ASTM D 5001 test. A similar result has been reported in a previous study. (10) The ASTM D 5001 BOCLE produces an oxidative wear mechanism that is easily halted by very low concentrations of corrosion inhibitor additives such as DCI 4A. The HFRR and ASTM D 6078 SLBOCLE tests require higher additive concentrations to eliminate adhesive wear of the metal surfaces.

In general, the fuel pretreatment processes with water had little measurable effect on wear. SLBOCLE tests were completely insensitive to all forms of water, including emulsified water and salt water, as shown in Figure 5. Some variation is present in the Gold Line data for scuff tests performed at 10-percent humidity, which is almost certainly due to random test variability. BOCLE tests performed according to ASTM D 5001 were also insensitive to the effects of dissolved water for all fuels except Jet A-1, as shown in Figure 4. Jet A-1 experienced a measurable increase in wear rate as relative humidity increased to 100 percent. Emulsification with deionized water increased wear with low lubricity fuels in the ASTM D 5001 BOCLE test, while emulsification with salt water resulted in reduced wear. Emulsification with either deionized or salt water had no effect on the wear rate observed with the better-lubricity fuels.

The wear test data obtained using the HFRR apparatus is shown in Figure 3. Wear in the HFRR for the low lubricity fuels was increased by exposure to either deionized water or sea water.

19

Emulsification with water did not result in increased wear and produced a slight decrease in wear with deionized water. Few other clear trends are apparent, indeed both Jet A-1 and Jet A-1 with 20 mg/L of DCI 4A showed a slight decrease in wear with increasing humidity, even though measured moisture content is constant. Examination of the unaveraged HFRR test data provided in Table F-1 indicates relatively poor repeatability between Runs 1 and 2. This variation may be due in part to the fuel preaeration system itself, although even standard HFRR tests performed under ambient conditions (highlighted in bold text in Table F-1) with ISOPAR-M show a test-to-test variation of 0.18 mm. In any event, much of the variation observed with the HFRR tests under conditions of controlled ambient humidity is likely to be due to random test variation rather than the effects of moisture.

The contact resistance measured between the reciprocating ball and the opposing flat in the HFRR apparatus is provided in Table F-3. In general, the contact resistance closely reflects the measured wear rate, i.e. a high contact resistance corresponds to a low rate of wear due to the formation of a strong, insulating, boundary lubricating film between the opposing surfaces. However, water emulsified into Cat 1-H produced a low contact resistance and low wear.

D.   Effect of Extended Aeration

In the previous sections, a number of fuel pretreatment processes were found to have little or no effect on measured moisture concentration. It is likely that the fuels became saturated during storage, eliminating the possibility of further increases in dissolved moisture content. However, recently produced fuel may contain little dissolved water due to the action of the refinery processes. The present section describes tests performed to define the effects of extended aeration using the BOCLE apparatus with fuel that was pretreated to remove dissolved water. Jet A-1 was selected for testing because it was the only fuel found to be sensitive to moisture. The Reference No. 2 fuel was selected due to its insensitivity to moisture effects on lubricity.

The predryed fuels were aerated at 0, 10 and 100 percent humidity for 48 hours in the stainless steel BOCLE reservoir following the conditions defined in ASTM D 5001. The results of laboratory scale wear tests following 0.5 and 48 hours of aeration are provided in Table F-9. The extended aeration had no effect on SLBOCLE wear tests with either fuel. HFRR tests performed with Jet A-1

20

showed a slight increased wear at high humidity, increasing further after 48 hours. Once again, however, the repeatability of the HFRR tests with the aeration process appears somewhat worse than normally expected.

Water concentration was defined following 0, 0.5, 1, 24 and 48 hours of aeration using the Accumet apparatus, with the results provided in Tables F-7 and F-8. The 0-hours sample was taken directly from the fuel storage container, while the 0.5 and 1-hour samples were taken before and after the BOCLE wear tests, respectively. The 48-hour sample was taken from the BOCLE reservoir following completion of the final wear tests. The results obtained using the ASTM D 5001 BOCLE procedure with Reference No. 2 and Jet A-1 fuels are plotted in Figures 6 and 7, respectively. In each instance, the data is plotted as a function of measured fuel water content in parts per million at either 0.5 or 1 and 48 hours. The "undried fuel" data represent the results of tests performed without extended aeration (as received fuel), either with or without bulk water present, i.e., the unaveraged results from tests at 0, 10, 50 and 100-percent Rh, two-percent deionized water in reservoir, and the deionized presoak data points. This data was previously plotted in Figure 5 and provided in Table F-4. The "undried fuel" data allows comparison between the results obtained with the dry fuel during extended aeration and the as received fuel tested under normal 15-minute aeration conditions. The "undried fuel" data does not include salt water tests nor the results of emulsified fuel/water tests. As expected, both predried fuels contained appreciably less water than the undried fuels used in the preceding tests.

The effects of aeration time on fuel moisture content are shown in Figures 8 and 9. The 48 hours of aeration had little effect on the moisture content of Reference No. 2 fuel, even at 100% humidity. In contrast, the extended aeration of Jet A-1 fuel at 100% humidity did produce a measurable increase in water content. However, in no instance did the additional 48 hours of aeration have a significant affect on lubricity as measured by the ASTM D 5001 test, as shown in Figures 6 and 7. Indeed, the lubricity of the predried Reference No 2 fuel samples was uniformly worse than that of the undried samples, possibly as a byproduct of the distillation process removing active components. In contrast, the lubricity of the predried Jet A-1 fuel was better than that of the undried samples, possibly due to its consistently low water content.
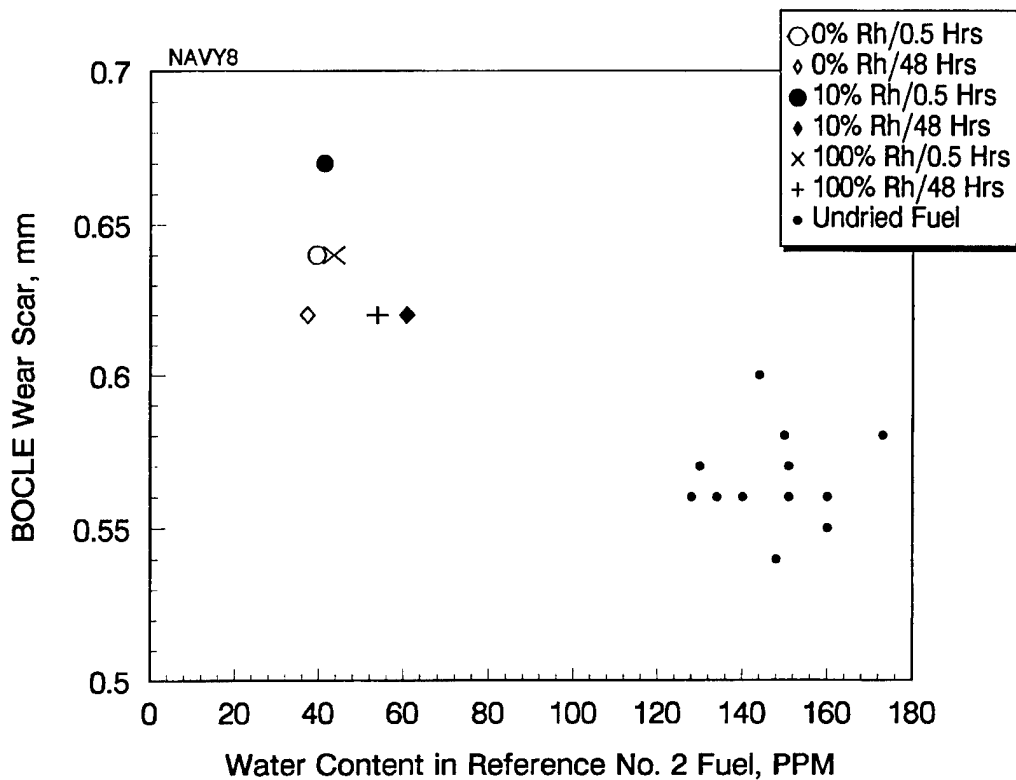
Figure 6. **Effect of Moisture Content and Extended Aeration on Wear of Reference No. 2 Diesel Fuel**
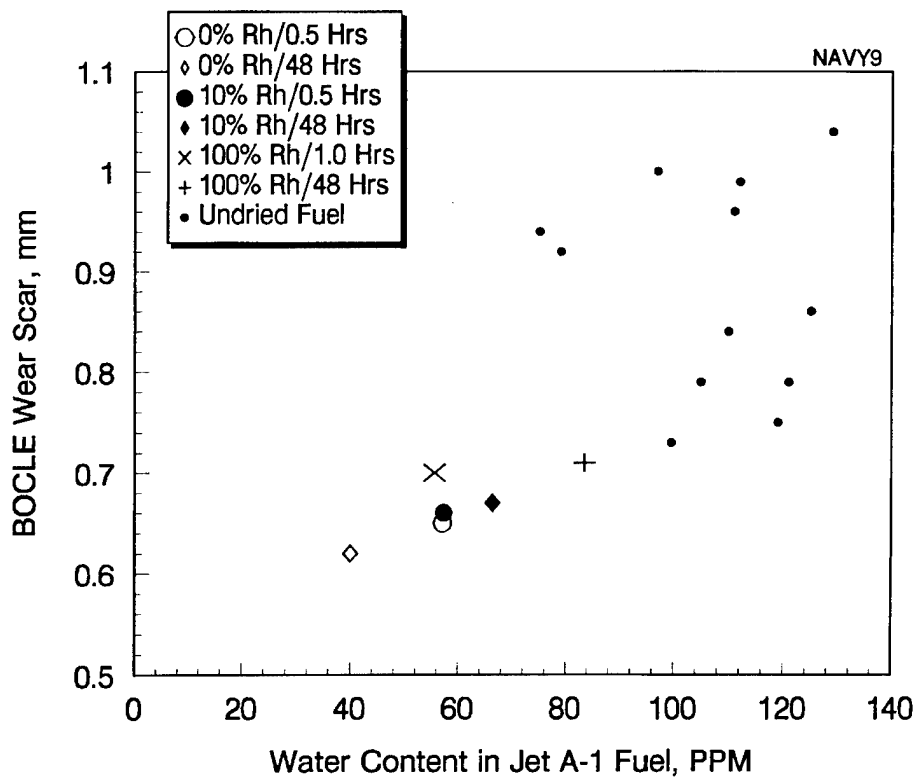
Figure 7. **Effect of Moisture Content and Extended Aeration on Wear of Reference Jet A-1 Fuel**

22

NAVY10
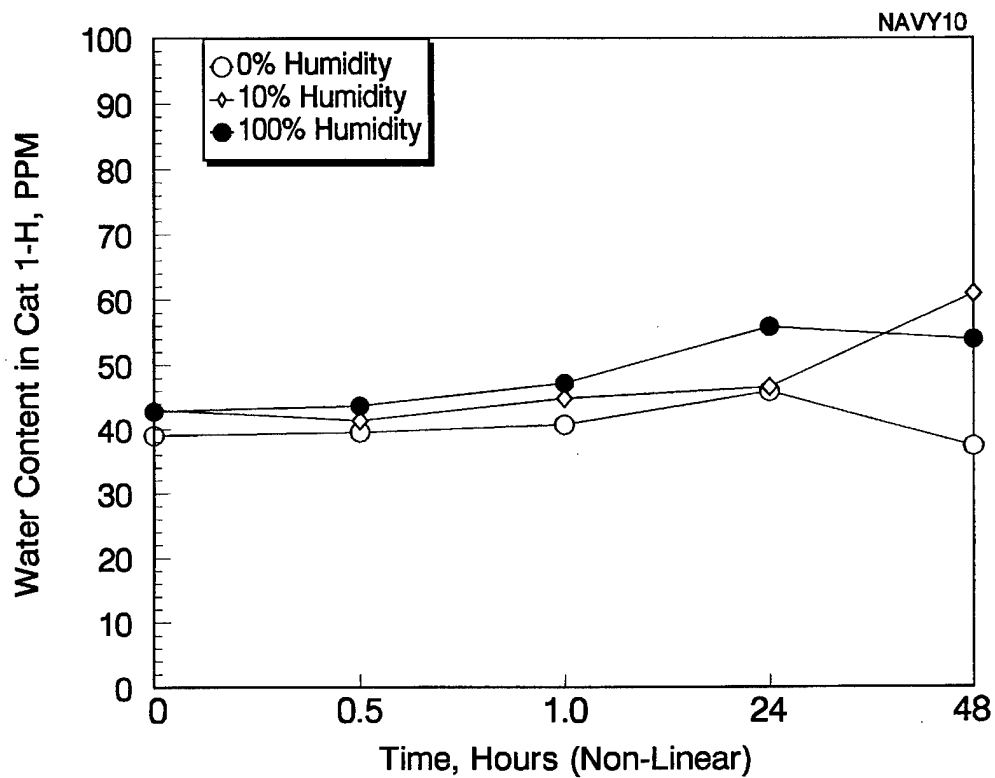
Figure 8. Effect of Aeration Time on Moisture Content of Reference No. 2 Diesel

NAVY11
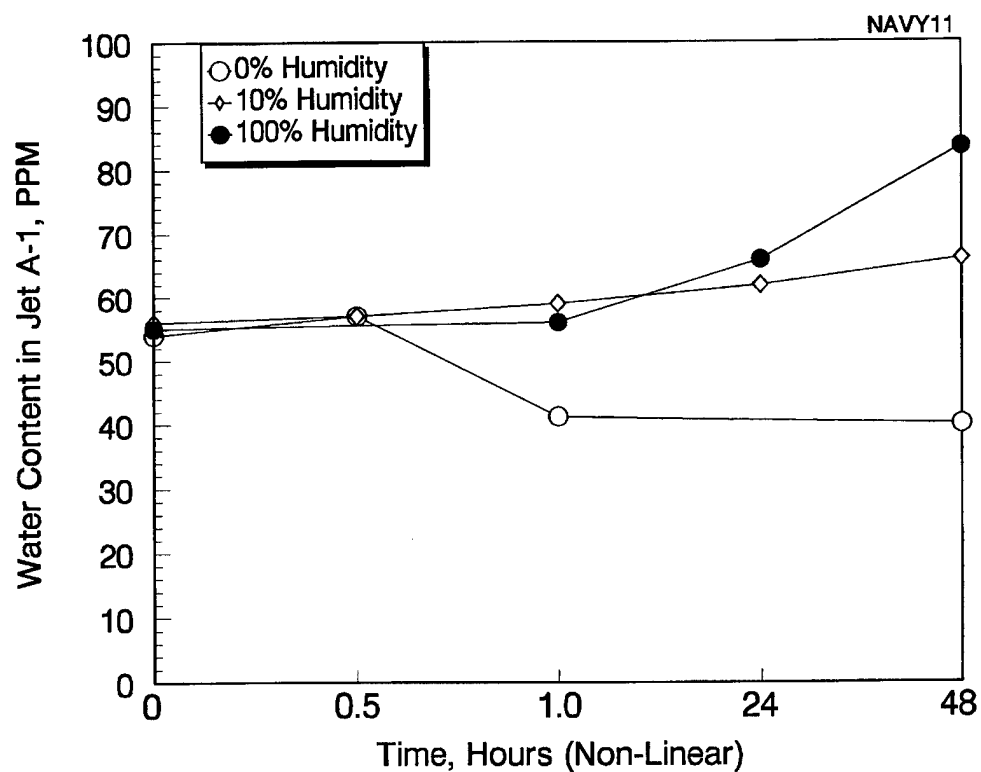
Figure 9. Effect of Aeration Time on Moisture Content of Jet A-1 Fuel

23

V. DISCUSSION

Fuel lubricity and wear resistance are two of the few properties that may be degraded by certain refinery processes.(11) Earlier publications indicate the likely presence of several wear mechanisms in fuel injection systems operated on highly refined fuels, including oxidative corrosion, as well as mild and severe adhesive wear.(12, 13) The relative importance of each wear mechanism was unclear. In addition, the importance of secondary effects, such as the availability of dissolved moisture, were also undefined. The effects of moisture would be particularly important in marine applications in which sea water is used for ballast as fuel is removed from the tanks and replaced by water. In the present study, wear tests were performed with six fuels using the BOCLE and HFRR apparatus. Three test procedures were used to replicate each of the wear mechanisms likely to exist in full-scale applications. In addition, the test fuels were exposed to varying amounts of both deionized and synthetic sea water, and the water concentration was measured using automated Karl Fischer titration.

The results indicate that for the vast majority of real fuels, exposure to increasing levels of ambient humidity and even bulk water have little effect on the concentration of dissolved water. Most fuels become saturated during normal storage, and it is relatively difficult to separate dissolved water from the fuel. As a result, the brief 15-minute pretest aeration used in the standard test procedures for the BOCLE and SLBOCLE has no measurable effect on water content. Indeed, little variation in fuel moisture content was observed during 48 hours of aeration at relative humidities ranging from 0 to 100 percent, as shown in Figures 6 and 7. Severe mechanical emulsification was the only mechanism capable of significantly affecting fuel moisture content. The difficulty in water removal may be due to the formation of an equilibrium between competing effects: the affinity of the aromatics and additives in the fuel to hold onto the water versus the ability of the treatment to remove it.

Wear rate with most fuels was also found to be largely unaffected by the different pretreatment processes with water. For fuels other than Jet A-1, only emulsification of 5 and 10-percent water had a truly significant effect on wear. These results are to be expected given the effects of the fuel pretreatment processes on the measured water content. However, no explanation is apparent for the

relatively low wear produced by synthetic sea water compared to deionized water in the ASTM D 5001 BOCLE wear test. The BOCLE provides a good measure of oxidative wear, which was expected to have been aggravated by the salt water solution.

The counterformal contact produced by the HFRR apparatus results in a contact stress of 27 MPa at a wear scar diameter of 0.15 mm. Contact stresses are appreciably higher with new specimens, typically resulting in adhesive wear of the opposing surfaces. However, it is widely recognized that many fuel-lubricated contacts also wear by an oxidative corrosion mechanism, which is aggravated by moisture. CEC procedure F-06-A-96 indicates that the HFRR result is sensitive to ambient water vapor pressure (AVP) and should be corrected using the following equation:

$$CWSD = WSD + 60x(1.4 - AVP) \qquad \text{(Equation 1)}$$

where

$$AVP = \frac{Rhx10^{\upsilon}}{760} \text{ in kPa}$$

$$\upsilon = 8.017352 - \frac{1705.984}{231.8636 + T}$$

RH = Relative humidity in percent close to the HFRR
T = Ambient temperature in °C close to the HFRR

The results shown in Figure 3 would indicate that this equation does not accurately reflect consistent effects of moisture. The HFRR results were largely insensitive to pretreatment with water, and little if any consistent relationship was observed between humidity and wear rate. In the present study, the fuel was sparged with air of known humidity, which would be expected to increase the potential effects of moisture. However, this approach does not rely on ambient humidity to affect fuel moisture content, and therefore not directly comparable to the CEC F-06-A-96 procedure. This may partially explain the poor repeatability of the HFRR test data. [An SwRI sponsored study, which accurately controls ambient humidity around the HFRR fuel reservoir, is in progress to resolve this issue.]

VI. CONCLUSIONS

The following conclusions may be drawn from the work performed in the present study

a)   Most fuels appear to reach the saturation limit for dissolved water during normal storage. The water content of these fuels is only slightly increased through exposure to bulk water.

b)   The water content of most fuels is between 60 and 200 PPM and is primarily dependent on the fuels' chemical and physical characteristics rather than their storage history.

c)   The 15-minute aeration period used in the ASTM D 5001 and ASTM D 6078 is not sufficient to significantly affect fuel moisture content. Indeed, only slight changes in water content were produced by 48 hours of aeration.

d)   Variations in aeration humidity had no effect on the SLBOCLE test performed according to ASTM D 6078. In addition, presoaking, soaking and emulsification with bulk water had no effect on the lubricity measurement.

e)   A slight increase in wear rate was produced by increasing aeration humidity with very low lubricity Jet A-1 in the ASTM D 5001 BOCLE wear test. All other fuels were insensitive to humidity.

f)   Variations in aeration humidity did not repeatably affect the wear observed in the HFRR apparatus.

g)   Exposure of the fuel to salt water did not normally increase wear more than would exposure to deionized water. Use of salt water reduced wear in some instances.

h)   Except for very poor lubricity fuels such as Jet A-1, there was no evidence of a correlation between measured water content in the fuel and lubricity.

VII. REFERENCES

1.   Department of Defense Directive 4140.43, Subject: "Fuel Standardization," Belvoir Research, Development and Engineering Center, Department of the Army, Fort Belvoir VA 22060-5606, (March 1988).

2.   Lacey, P.I., and Erwin, J., "Test Plan for Effect of Refining Severity on the Lubricity of NATO F-76 Fuel," U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI), Southwest Research Institute, January 1996.

3.	Wear Control Handbook, Peterson, M.B., Winer, W.O., ed., ASME, United Engineering Center, 345 East 47th Street, New York, NY 10017, (1980).

4.	Lacey, P.I., "Wear With Low-Lubricity Fuels, Part I: Development of a Wear-Mapping Technique," *Wear*, 160, pp. 325–332, (1993).

5.	Lacey, P.I., "Wear With Low-Lubricity Fuels, Part II: Correlation Between Wear Maps and Pump Components," *Wear*, 160, pp. 333–343, (1993).

6.	Lacey, P.I. and Lestz, S.J., "Fuel Lubricity Requirements for Diesel Injection Systems," Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, San Antonio, TX, Interim Report BFLRF No. 270, (AD A235972), available from Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22314, (February 1991).

7.	American Society for Testing and Materials Method D 5001-89, "Test Method for Measurement of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE), ASTM, 1916 Race Street, Philadelphia, PA, (1989).

8.	American Standard for Testing and Materials Standard D 6078, "Standard Test Method for Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)," ASTM, 1916 Race Street, Philadelphia, PA, 1997.

9.	American Standard for Testing and Materials Standard D 6079, "Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High Frequency Reciprocating Rig (HFRR)," ASTM, 1916 Race Street, Philadelphia, PA, 1997.

10.	Lacey, P.I., "The Relationship Between Fuel Lubricity and Diesel Injection System Wear," Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, San Antonio, TX, Interim Report BFLRF No. 275, (AD A247927), available from Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22314, (January 1992).

11.	"Aviation Fuel Lubricity Evaluation," Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA 30346, CRC Report No. 560, (July 1988).

12.	Lacey, P.I. and Lestz, S.J., "Effect of Low-Lubricity Fuels on Diesel Injection Pumps-Part I: Field Performance," SAE Paper 920823, Society of Automotive Engineers, 400 Commonwealth Drive, Warrendale, PA 15096-0001, (1992).

13.	Lacey, P.I., "Wear Mechanism Evaluation and Measurement in the Rotary Diesel Fuel Injection System," Belvoir Fuels and Lubricants Research Facility, Southwest Research Institute, San Antonio, TX, Interim Report BFLRF No. 286, available from Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22314, (January 1993).

14.   Military Specification MIL-I-25017E, "Inhibitor, Corrosion/Lubricity Improver, Fuel Soluble (Metric)," available from Standardization Documents Order Desk, Building 4D, 700 Robbins Avenue Philadelphia, PA 19111-5094, (15 June 1989).

15.   Coordinating European Council, Test Method CEC F-06-A-96, "Measurement of Diesel Fuel Lubricity," CEC Secretariat, Mandou Plaza 25th Floor, Place Madou 1, B-1210 Brussels, Belgium, 1996.

APPENDIX A

Photographs of Test Apparatus

A-2
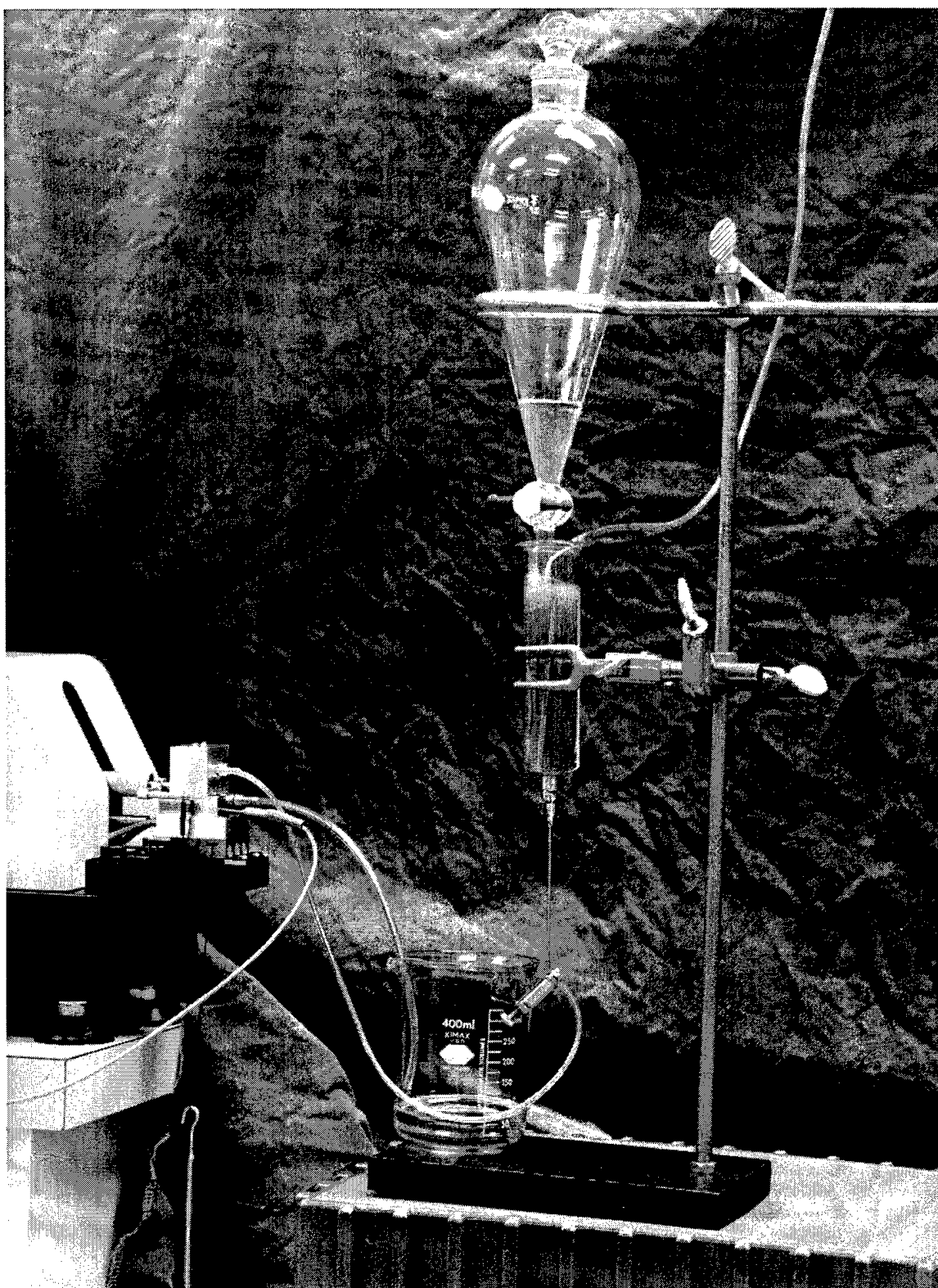
Figure A-1. <u>High Frequency Reciprocating Rig with Fuel Aeration Apparatus</u>

Figure A-2: <u>Overview of Ball on Cylinder Lubricity Evaluator</u>

Figure A-3. The Aquatest IV Apparatus
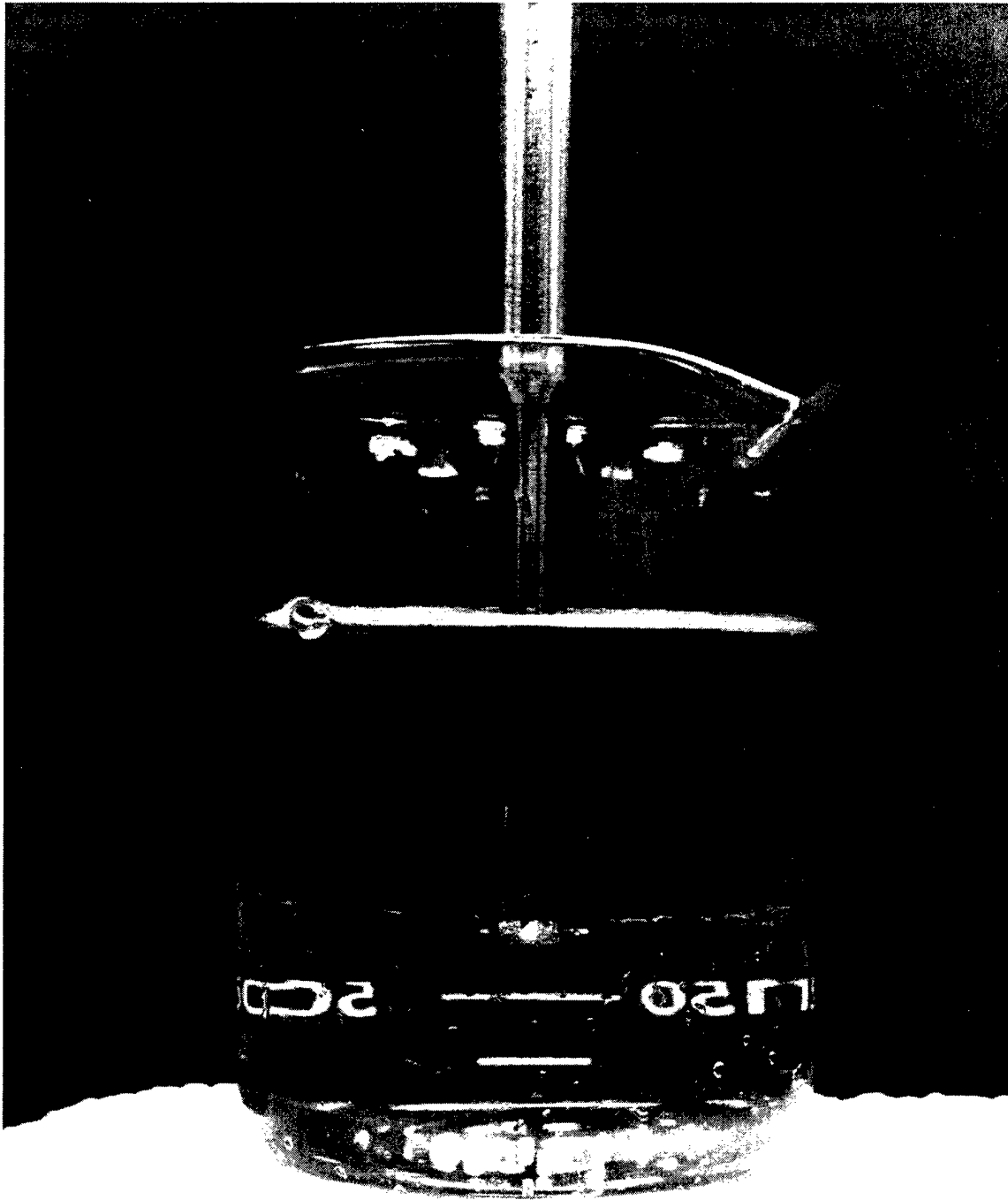
Figure A-4A. Fuel and Water Prior to Emulsification
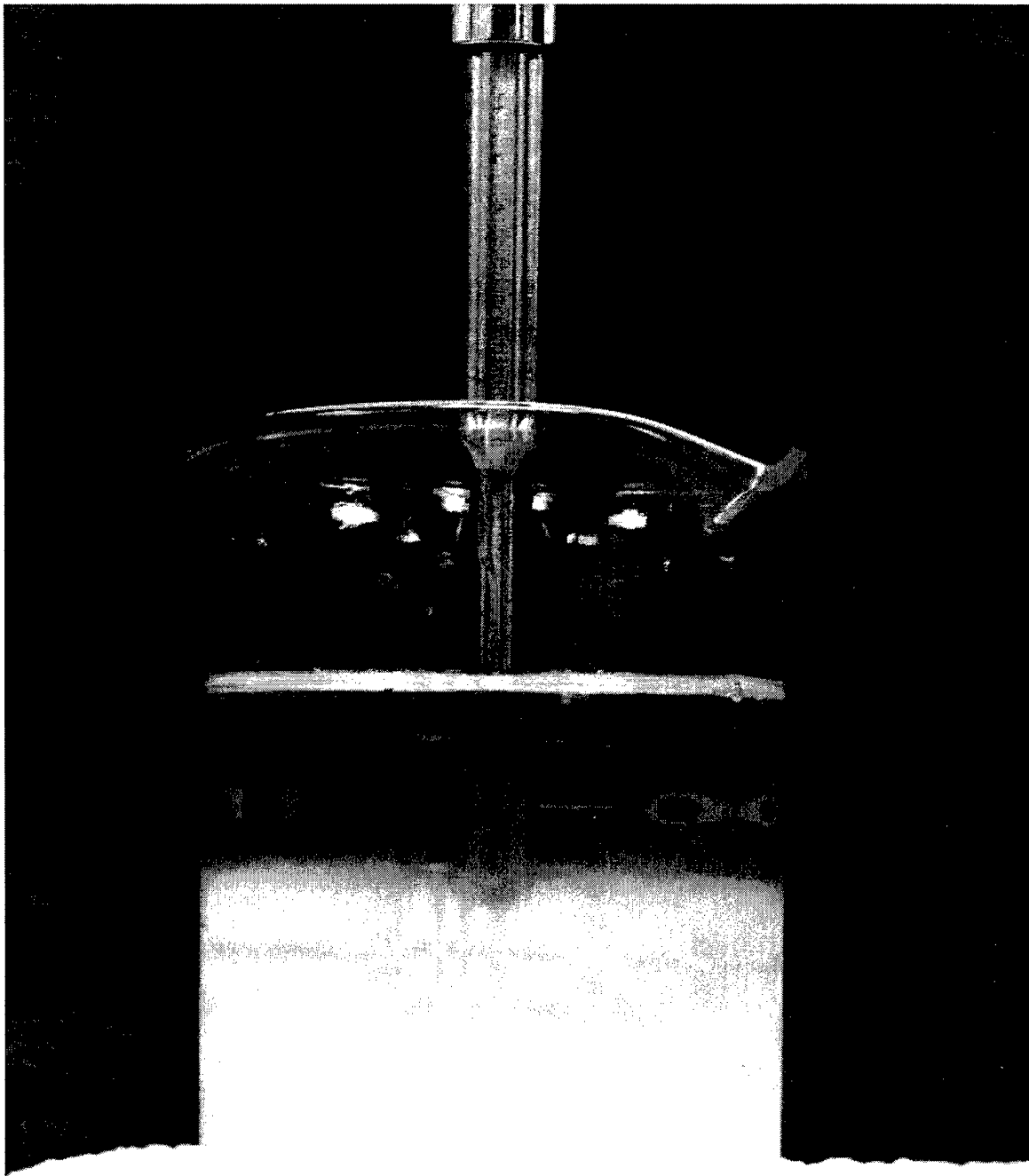
Figure A-4B: <u>Fuel and Water after 5 seconds of emulsification</u>
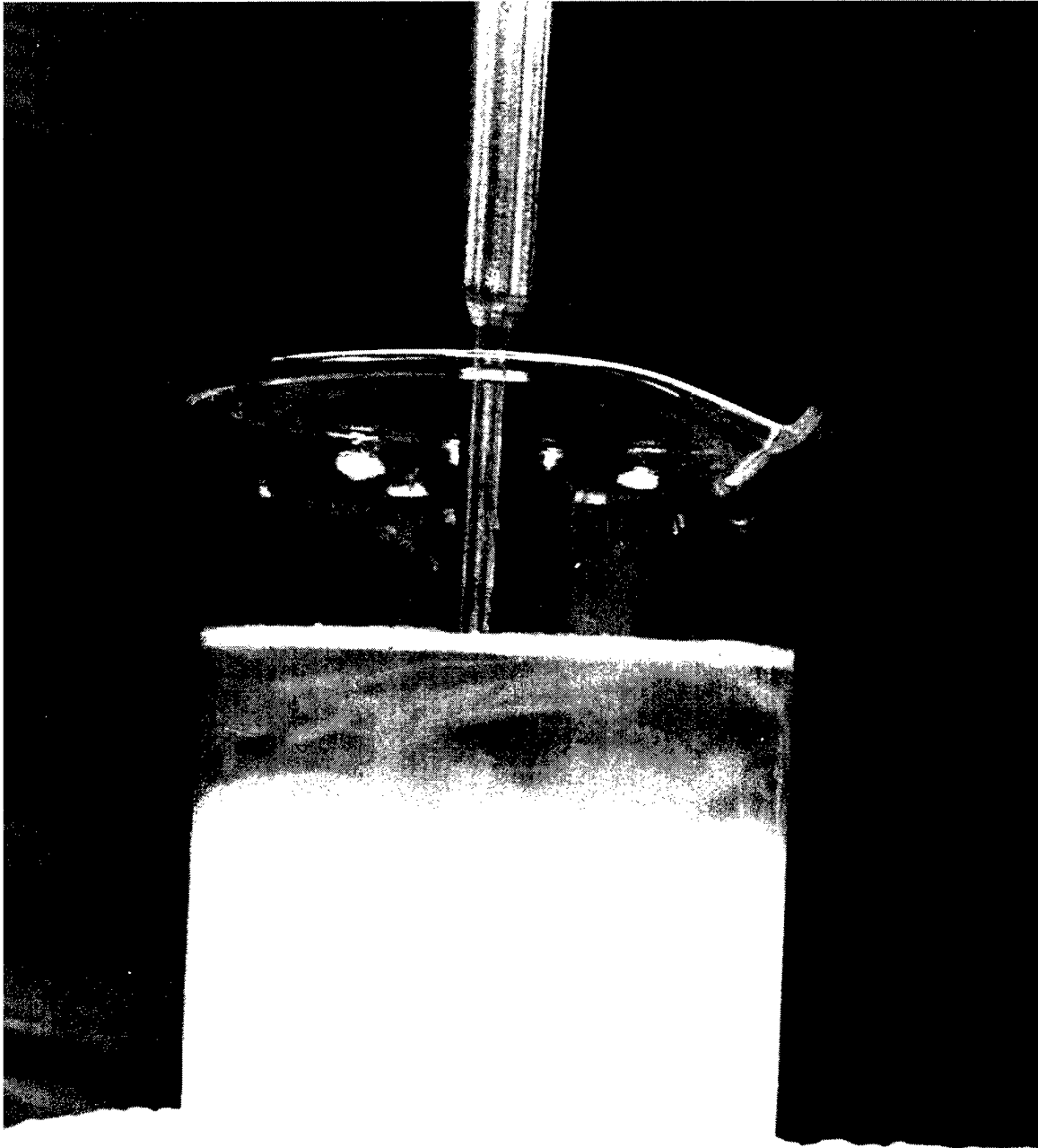
Figure A-4C. Fuel and water after 10 seconds of emulsification
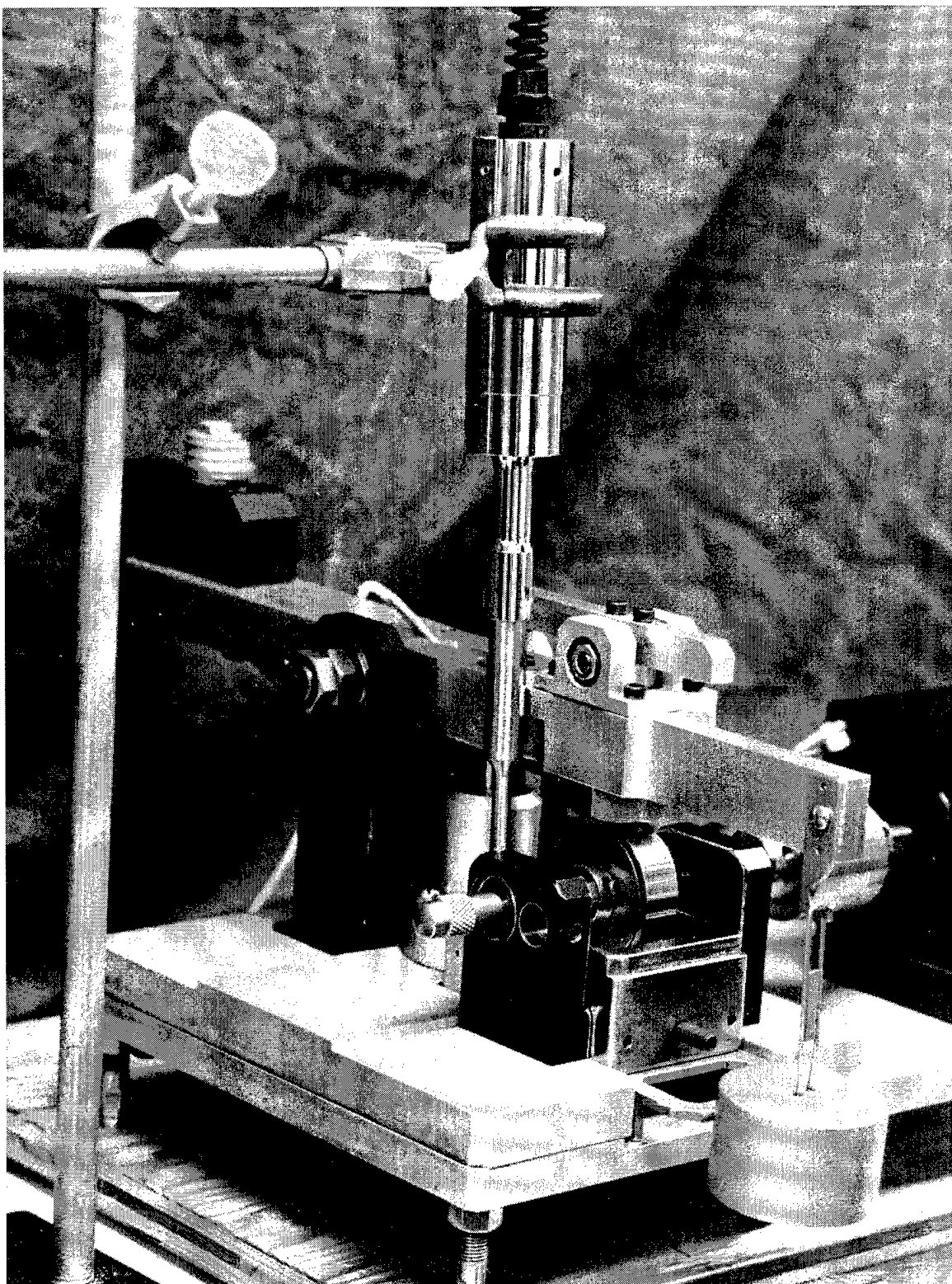
Figure A-5. Detail View of BOCLE Apparatus with Emulsifier Probe in Place

A-9
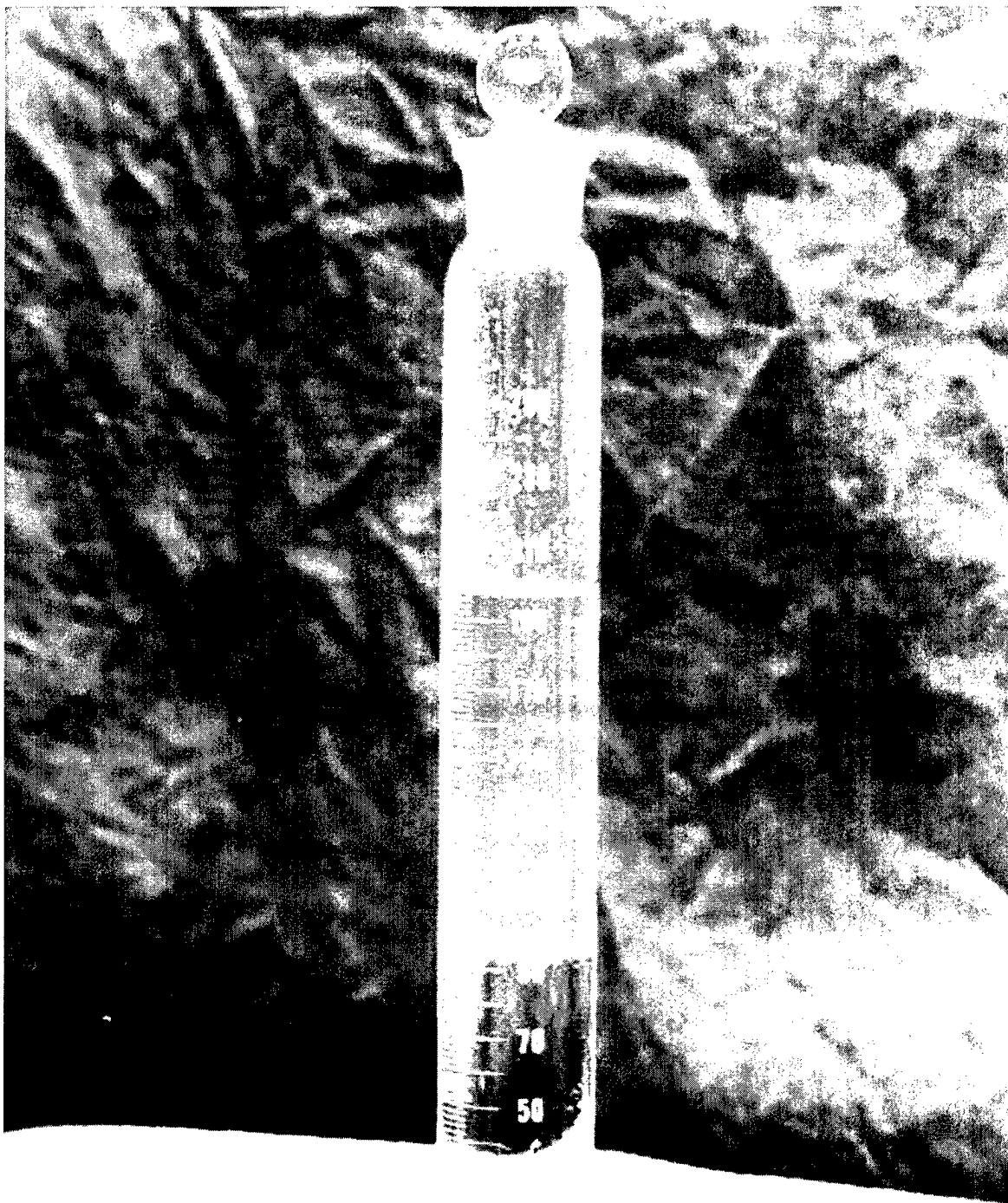
Figure A-6. View of Graduated Beaker used to Presoak Fuel/Water Mixture

APPENDIX B

Test Procedure for the U.S. Army Scuffing Load Wear Test

THE U.S. ARMY SCUFFING LOAD WEAR TEST

**Suggested Test Procedure for Measurement of Scuffing Load Capacity
Using the Ball-on-Cylinder Lubricity Evaluator (BOCLE)***

01 January 1994

---

* **Note:** The following is a draft test procedure. This test procedure is based on
ASTM D 5001 and contains changes made solely by the U.S. Army TARDEC Fuels
and Lubricants Research Facility (TFLRF). Comments, additions, and changes
should be addressed to Dr. P.I. Lacey, U.S. Army TARDEC Fuels and Lubricants
Research Facility (SwRI), Southwest Research Institute, P.O. Drawer 28510, San
Antonio, Texas 78228-0510.

1. Scope

1.1.   This test method assesses the severe wear aspects of the boundary lubrication properties of fuels intended for use in compression ignition equipment on rubbing steel surfaces.

1.2.   The values stated in SI units are to be regarded as the standard.

2. Referenced Documents

2.1.   *ASTM Standards:*

D 329 Specification for Acetone[1]

D 770 Specification for Isopropyl Alcohol[1]

D 1016 Test Method for Purity of Hydrocarbons From Freezing Points[2]

D 4306 Practice for Sampling Aviation Fuel for Tests Affected by Trace Contamination[3]

2.2.   *Military Specification:*

MIL-I-25017, Inhibitor, Corrosion/Lubricity Improver, Fuel Soluble[4]

2.3.   *American Iron and Steel Institute Standard:*

AISI E-52100 Chromium Alloy Steel[5]

2.4.   *American National Standards Institute Standard:*

ANSI B3.12, Metal Balls[6]

2.5.   *Society of Automotive Engineers Standard:*

SAE 8720 Steel[7]

3. Terminology

3.1.   *Descriptions of Terms Specific to This Procedure:*

3.1.1.   *Cylinder*—the polished test ring and mandrel assembly.

3.1.2.   *Lubricity*—a property of the fluid, measured by the minimum applied load, in grams, that will produce a transition from mild boundary lubricated wear to adhesive scuffing between a stationary ball and a fluid-wetted rotating ring operating under closely controlled conditions.

4. Summary of Test Method

4.1.   The fluid under test is placed in a test reservoir in which atmospheric air is maintained at 50% relative humidity. A nonrotating steel ball is held in a vertically mounted chuck and forced against an axially mounted *polished* steel ring. The applied load is increased until a disproportionate change in friction and wear is observed. Any sequence of increasing loads may be selected to most efficiently define

---

[1]   *Annual Book of ASTM Standards,* Vol 06.03.

[2]   *Annual Book of ASTM Standards,* Vols 05.01 and 06.03.

[3]   *Annual Book of ASTM Standards,* Vol 05.03.

[4]   Available from Naval Publications and Form Center, 5801 Tabor Ave., Philadelphia, PA 19120.

[5]   Available from American Iron and Steel Institute, 1000 16th Street, NW, Washington, DC 20036.

[6]   Available from American National Standards Institute, 1430 Broadway, New York, NY 10018.

[7]   Available from Society of Automotive Engineers, Inc., 400 Commonwealth Ave., Warren, PA 15096.

the point at which either friction or wear exceeds defined limits. The fuel is not renewed between load increments during a normal test sequence. The test cylinder is rotated at a fixed speed while being partially immersed in the fluid reservoir. This partial immersion maintains the cylinder in a wet condition and continuously transports the test fluid to the ball/cylinder interface. The minimum applied load required to produce a transition to severe friction and wear is a measure of the fluid-lubricating properties.

5. Significance and Use

5.1.   Severe wear resulting in shortened life of components on compression-ignition engines such as fuel pumps has sometimes been ascribed to lack of lubricity in highly refined fuel.

5.2.   The relationship of test results to rotary fuel injection pump distress due to wear has been demonstrated for some fuel/hardware combinations in which boundary lubrication is a factor in the operation of the component.

5.3.   The scuffing load capacity in the Ball-on-Cylinder Lubricity Evaluator (BOCLE) test is sensitive to contamination of the fluids and test materials, the presence of oxygen and water in the atmosphere, and the temperature of the test. Lubricity measurements are also sensitive to trace materials acquired during sampling and storage. Containers specified in Practice D 4306 shall be used.

5.4.   Initial tests with many different procedures indicate that correlation achieved with full-scale equipment may be affected by viscosity, particularly if viscosity is below approximately 1.8 cSt at 40°C.

5.5   *Simplification of Procedure*

5.5.1.   If desired, the incremental-load procedure described in Section 10 may be modified to a single-load test at a test load to be defined.

5.5.2.   The single-load test has been found to approximate full-scale equipment needs and to provide a simple pass/fail result.

5.5.3.   The single-load test does not provide a quantitative ranking of fuels in either the pass or fail categories.

6. Apparatus

6.1.   *Ball-on-Cylinder Lubricity Evaluator (BOCLE).*

6.1.1.   The test requirements are listed in TABLE C-1.[8]

6.1.2.   If possible, the apparatus should facilitate accurate measurement of tangential friction. However, accurate determination of scuffing load capacity is possible without friction measurement.

6.1.3.   The inclusion of a small splash guard within the fluid reservoir is necessary to prevent loss of fluid from the joint between the reservoir cover and reservoir.

6.2.   *Constant Temperature Bath-Circulator,* capable of maintaining the fluid sample at 25° ± 1°C when circulating coolant through the base of the sample reservoir.

---

[8]   BOCLE units, BOC 100, made by InterAv, Inc., P.O. Box 792228, San Antonio, TX 78279 have been found to be satisfactory.

B-5

TABLE B-1. Operating Conditions

Fluid Volume	50 ± 1.0 mL
Fluid Temperature	25° ± 1°C
Conditioned Air*	50 ± 1% relative humidity at 25° ± 1°C

Fluid pretreatment 0.50 L/min air flowing through and 3.3 L/min over the fluid for 15 min.

8.1 ft³/hr = 3.8 L/min.

Fluid test conditions 3.8 L/min flowing over the fluid.

Applied Load	
Break-In Period	500 g
Incremental-Load Test	500 to 8,000 g
Single-Load Test	To be defined
Cylinder Rotational Speed	525 ± 1 r/min
Test Duration	
Break-In Period	30 sec
Scuff Tests	60 sec

* Note: 50% humidity should be achieved using <u>equal</u> volumes of dry and saturated air.

6.3.   *Microscope,* capable of 100× magnification in graduations of 0.1 mm and incremented in divisions of 0.01 mm.

6.3.1.   *Glass Slide Micrometer,* with a scale ruled in 0.01 mm divisions.[9]

6.4.   *Cleaning Bath*—Ultrasonic seamless stainless steel tank with a capacity of 1.9 L (0.5 gal) and a cleaning power of 40 W.

7.   Reagents and Materials

7.1.   *Test Ring,* of SAE 8720 steel, having a Rockwell hardness "C" scale (HRC) number of 58 to 62 and a surface finish of 0.015 μm root mean square. The remaining dimensions are similar to that described in ASTM D 5001.[10]

7.2.   *Mandrel,* a 10° tapered short cylindrical section used for holding test ring.[11]

---

[9]   Catalog No. 31-16-99 from Bausch and Lomb. Inc. has been found satisfactory. A certificate of traceability from the National Institute of Standards and Technology is available.

[10]   Test Rings, Part No. F25061 from Falex Corp., 2055 Comprehensive Drive, Aurora, IL 60505, have been found satisfactory if polished to the required surface finish using only the procedure defined by the U.S. Army Belvoir Fuels and Lubricants Research Facility, P.O. Drawer 28510, San Antonio, TX 78228. Correct surface finish is central to test accuracy.

[11]   Mandrel, Part No. M-O from Falex Corp., or P/N BOC-2101 from InterAv. Inc., P.O. Box 792228, San Antonio, TX 78279, has been found satisfactory.

7.3. *Test Ball,* chrome alloy steel, made from AISI standard steel No. E-52100, with a diameter of 12.7 mm (0.5 in.) grade 5 to 10 EP finish. The balls are described in ANSI Specification B3.12. The extra-polish finish is not described in that specification. The HRC shall be 64 to 66, a closer limit than found in the ANSI requirement.[12]

7.4. *Compressed Air,* containing less than 0.1 PPM hydrocarbons and 50 PPM water.

7.5. *Desiccator,* containing a nonindicating drying agent, capable of storing test rings, balls, and hardware.

7.6. *Gloves,* clean, lint-free, cotton, disposable.

7.7. *Wiper,* wiping tissue, light-duty, lint-free, hydrocarbon-free, disposable.

7.8. *Isooctane,* conforming to Test Method D 1016, 95% purity minimum, 2,2,4-trimethylpentane.

7.9. *Isopropyl Alcohol,* conforming to Specification D 770.

7.10. *Acetone,* conforming to Specification D 329.

7.11. *Reference Fluids.*

7.11.1. *Fluid A*—Shall be Reference No. 2 (Cat 1-H) diesel fuel.[13] Store in borosilicate glass with an aluminum foil lined insert cap. Store in dark area.

7.11.2. *Fluid B*—Shall be a narrow-cut isoparaffinic solvent.[14]

8. Preparation of Apparatus

8.1. *Cleaning of Apparatus and Test Components:*

8.1.1. *Test Rings:*

8.1.1.1. The test rings shall be partially stripped of any wax-like protective coatings by manually rubbing them with rags or paper towels saturated with isooctane.

8.1.1.2. Place partially cleaned rings in a clean 500-mL beaker. Transfer a sufficient volume of a 1 to 1 mixture of isooctane and isopropyl alcohol to the beaker such that the test rings are completely covered.

8.1.1.3. Place beaker in ultrasonic cleaner and turn on for 15 min.

8.1.1.4. Remove test rings and repeat ultrasonic cleaning cycle of 8.1.1.2 and 8.1.1.3 with a clean beaker and fresh solvents.

8.1.1.5. Handle all clean test rings with clean forceps or disposable gloves. Remove test rings from beaker and rinse with isooctane. Dry. Rinse with acetone.

NOTE 1: Drying operations can be accomplished using a compressed air (7.4) jet at 140 to 210 kPa (20 to 30 psi) pressure.

8.1.1.6. Dry and store in a desiccator.

---

[12] Test Balls, SKF Swedish, Part No. 310995A, RB 12.7, grade 5 to 10 EP Finish, AISI 52100 Alloy from SKF Industries, Component Systems, 1690 East Race Street, Allentown, PA 90653, have been found satisfactory.

[13] Available from Howell Hydrocarbons, P.O. Box 429, Channelview, TX 77530.

[14] Solvent is ISOPAR M, manufactured by the Exxon Company, USA, P.O. Box 2180, Houston, TX 77001.

8.1.2.   *Test Balls, as Received.*

8.1.2.1.   Place balls in 300-mL beaker.   Transfer a sufficient volume of a 1 to 1 mixture of isooctane and isopropyl alcohol to the beaker such that the test balls are completely covered by the cleaning solvent.

NOTE 2: Approximately a 5-day supply can be processed at one time.

8.1.2.2.   Place beaker in ultrasonic cleaner and turn on for 15 min.

8.1.2.3.   Repeat the cleaning cycle of 8.1.2.1 and 8.1.2.2 with a clean beaker and fresh solvent.

8.1.2.4.   Remove and rinse with isooctane, dry, rinse with acetone.

8.1.2.5.   Dry and store in a desiccator.

8.1.3.   *Reservoir, Reservoir Cover, Ball Chuck, Ball Lock Ring, and Ring Mandrel Assembly Components:*

8.1.3.1.   Rinse with isooctane.

8.1.3.2.   Clean for 5 min. in an ultrasonic cleaner with a 1 to 1 mixture of isooctane and isopropyl alcohol.

8.1.3.3.   Remove and rinse with isooctane, dry, rinse with acetone.

8.1.3.4.   Dry and store in a desiccator.

8.1.4.   *Hardware:*

8.1.4.1.   The hardware and utensils, that is, shaft, wrenches, and tweezers, that come in contact with the test fluid shall be cleaned by washing thoroughly with isooctane and wiping with a lint-free cloth.

8.1.4.2.   Store parts in desiccator when not in use.

8.1.5.   *After Test:*

8.1.5.1.   Remove reservoir and cylinder.

8.1.5.2.   Disassemble components and clean for 5 min. in an ultrasonic cleaner using a 1 to 1 mixture of isooctane and isopropyl alcohol.   Rinse with isooctane, dry, rinse with acetone. Reassemble components.

8.1.5.3.   Dry and store in a desiccator.

8.1.5.4.   Care shall be taken to ensure that the fuel aeration tube is rinsed and dried during the cleaning procedure.   Store parts in desiccator when not in use.

9.   Calibration and Standardization

9.1.   Visually inspect test balls and rings before each test.   Discard specimens that exhibit pits, corrosion, or surface abnormalities.

9.2.   *Reference Fluids:*

9.2.1.   Test each new batch of the reference fluids and verify machine accuracy in accordance with Section 10.

9.2.2.   The machine calibration should be verified once every twelve tests.

9.2.3. If desired, the test need only be performed at the two loads defined in Section 9.2.6 to verify test performance and accuracy.

9.2.4. Additional tests are necessary if the scuffing load capacities on Reference Fluids A and B lie outside the acceptable range.

9.2.5. Calculate the scuffing load capacity (SLC) in accordance with Section 13.0.

9.2.6. The following reference fluid values are preliminary: No scuffing should be produced at 4,500 and 900 g with Reference Fluids A and B, respectively. Scuffing should be produced at 5,100 and 1,400 g with Reference Fluids A and B, respectively.

9.3. *Leveling of Load Arm:*

9.3.1. The level of the load arm shall be inspected prior to each test. Level the motor platform by use of the circular bubble level and adjustable stainless steel legs.

9.3.2. Install a test ball in the retaining nut as described in Section 10.4.

9.3.3. Lower load arm. Attach required weight to end of load beam. Lower ball onto ring manually or by use of arm actuator switch.

9.3.4. Check level on top of load arm. The indicator bubble shall be centered in the middle of the two lines. If required, adjust the retaining nut screw to achieve a level load arm.

9.4. *Assembly of Cylinder:*

9.4.1. Place a clean test ring on the mandrel and bolt the back plate to the mandrel.

10. Procedure

10.1. The summary of test conditions is included in TABLE B-1.

10.1.2. The test procedure described in Sections 10.2 through 10.29 is repeated with a finite load change until scuffing is observed, as described in Section 13.

10.1.3. Any desired sequence of load increments may be selected to most rapidly converge on the scuffing transition. The loading sequence provided at the end of this procedure is strongly recommended.

10.1.4. The test fluid should be replaced/aerated and the apparatus thoroughly cleaned after every eighth load increment.

10.2. *Installation of Cleaned Test Cylinder:*

NOTE 3: The BOCLE is very sensitive to contamination problems.

10.2.1. The greatest care shall be taken to adhere strictly to cleanliness requirements and to the specified cleaning procedures. During handling and installation procedures, protect cleaned test parts (cylinder, balls, reservoir, and reservoir cover) from contamination by wearing clean cotton gloves.

10.2.2. Rinse shaft with isooctane and wipe with disposable wiper.

10.2.3. Push the shaft through the left bearing and support bracket.

10.2.4. Hold the cylinder with the set screw hub facing left. Push the shaft through the cylinder bore, through the right bearing support bracket, and into the coupling as far as the shaft will go.

10.2.5. Align the coupling set screw with the flat keyway side of the cylinder shaft. Tighten set screw.

B-9

10.2.6.   Set micrometer at 2.50 mm and slide cylinder to the left until it is firmly against micrometer probe. Ensure that cylinder set screw is directed toward the keyway (flat surface of shaft) and tighten set screw.

10.2.7.   Back micrometer probe away from the cylinder before drive motor is engaged.

10.3.   Record on the data sheet the ring number, if assigned, and the position of the test cylinder as indicated by the micrometer. The first and last wear tracks on a ring shall be approximately 1 mm in from either side.

10.3.1.   For subsequent tests, reset cylinder to a new test position with the micrometer.

10.3.2.   If the fuel is not to be changed, the cylinder should be adjusted by loosening the coupling set screw rather than at the mandrel, to minimize atmospheric contamination between tests. Unnecessary removal of the reservoir cover should be avoided after the initial aeration is completed.

10.3.3.   If the fuel sample is to be changed/aerated, then the adjustment may be made at the mandrel. (Fuel is changed only after eight consecutive tests.)

10.3.4.   The new position is to be 0.75 mm from the last wear track on the ring and noted on the data sheet.

10.3.5.   After tightening the coupling set screw to lock the cylinder/shaft in a new test position, the micrometer probe should be backed off, then advanced to the cylinder again. Check micrometer reading to ensure correct track spacing. Readjust position, if required. When the correct ring position is ensured, back the micrometer probe away from the cylinder.

10.4.   Install a clean test ball prior to each test by first placing the ball in the retaining nut, followed by the blue retaining ring. Screw retaining nut onto the threaded chuck located on the load arm and hand tighten.

10.5.   Secure the load beam in the Up position by insertion of the blue pin.

10.6.   If necessary, install the clean reservoir. Install the blue spacing platform by raising the reservoir. Slide blue spacer platform into position under the reservoir. Place thermocouple in the hole provided at the rear left side of the reservoir. Insert splash guards.

10.7.   Check load beam level. Adjust, if necessary.

10.8.   If necessary, supply test fluid in accordance with Practice D 4306. Transfer 50 ± 1 mL of the test fluid to the reservoir. Place cleaned reservoir cover in position and attach the 1/4 to 1/8 in. air lines to reservoir cover.

10.9.   Move power switch to On position.

10.10.   Turn on compressed air cylinder. Adjust the delivery pressure to 210 to 350 kPa (30 to 50 psi) and the console air pressure to approximately 100 kPa (14.5 psi).

10.11.   Lower load beam by pulling blue pull pin. Do not allow the ball specimen to contact the ring.

10.12.   Start rotation of cylinder by switching motor drive to On. Set rotation to 525 ± 1 r/min.

10.13.   Using the flowmeters that control the wet and dry airflows, adjust conditioned airflow to read 3.8 L/min. Maintain 50 ± 0.2% relative humidity.

NOTE 4: 50% relative humidity should require approximately equal volumes of wet and dry air.

10.14. Adjust reservoir temperature as required until temperature stabilizes at 25° ± 1°C. Adjust thermostat of the heat exchanger circulating bath to obtain the required temperature.

10.15. If necessary, set fuel aeration timer for 15 min and adjust fuel aeration flowmeter to 0.5 L/min. (First test in load sequence only.)

10.16. At completion of aeration (if performed), the whistle will sound and aeration will cease. Continue 3.8 L/min flow through the reservoir.

10.17. *Break-In*

    10.17.1. Place 500-g load on load arm.

    10.17.2. Gently lower load arm. The pneumatic lift arm actuator must not be used.

    10.17.3. Switch timer on for 30 seconds.

    10.17.4. At the end of 30 seconds, the whistle will sound, and the test load must be immediately removed.

10.18. Switch on chart recorder to measure friction trace (if available).

10.19. Check all test condition readouts and adjust as necessary. Record all necessary information on data sheet.

10.20. Place required load on load arm. Do not replace test ball or adjust test cylinder. (See the end of this procedure for suggested loading sequence.)

10.21. Gently lower load arm. The pneumatic lift arm actuator must not be used.

10.22. Switch timer on for 60 seconds.

10.23. At the end of 60 seconds, the whistle will sound, and the test load must be immediately removed.

10.24. Manually remove test weight. Lift test load arm up and secure with blue pull pin.

10.25. Do not remove reservoir cover unless fuel is to be replaced. If fuel is not to be replaced, wipe revolving ring with an unused disposable lint free cloth to remove residue from the test ring. Turn motor drive and power switch to Off.

10.26. Remove test ball from locking nut. Do not remove ball from blue retaining ring. Wipe ball clean with disposable wipe prior to microscopic examination. Replace with new ball.

10.27. Measure the MAXIMUM friction coefficient (if available) and wear scar diameter as described in Section 11.

10.28. Determine if scuffing has occurred at the last applied load, as defined in Section 13.

10.29. If scuffing has not occurred, repeat from Section 10.2 with appropriate load increment as defined at the end of this procedure.

11. Measurement of Wear Scar and Friction

11.1. *Wear Scar Measurement*

    11.1.1. Turn on microscope light and position test ball under microscope at 100× magnification.

    11.1.2. Focus microscope and adjust stage such that wear scar is centered within the field of view.

11.1.3.   Align the wear scar to a divisional point of reference on the numerical scale with the mechanical stage controls. Measure the major axis to the nearest 0.01 mm. Record the readings on the data sheet.

11.1.4.   Align the wear scar to a divisional point of reference on the numerical scale with the mechanical stage controls. Measure the minor axis to the nearest 0.01 mm. Record the readings on the data sheet.

11.1.5.   Record condition of wear area if different from the reference standard test, that is, debris color, unusual particles or wear pattern, visible galling, etc., and presence of particles in the reservoir.

11.2.   *Friction Measurement*

11.2.1.   Measure <u>maximum</u> tangential friction force in grams from output on stripchart recorder.

11.2.2.   Calculate friction coefficient as described in Section 12.

11.2.3.   Record applied load and friction coefficient.

12. Calculation

12.1.   Calculate the wear scar diameter as follows:

where: *WSD* = Wear scar diameter, mm

M   = Major axis, mm,
N   = Minor axis, mm.

12.2   Calculate the maximum friction coefficient as follows

$$\mu = \frac{Ft}{Fn} \qquad\qquad \text{(Eq. 2)}$$

where: μ = Coefficient of Friction,

Ft   = Maximum tangential friction force, g,

Fn = Contact load, g (= 2× applied Load).

13. Adhesive Scuffing

13.1.   Scuffing may be defined as the transition from mild boundary lubricated wear or oxidative corrosion wear to more severe adhesive wear.

13.2.   The onset of scuffing is accompanied by a marked increase in both friction and wear. Typical friction traces are provided in Fig. C-1.

13.2.1. Scuffing is considered to occur if the friction coefficient exceeds 0.175 at any time during the test.

13.2.2. Scuffing is considered to occur if the plotted friction coefficient or wear scar diameter increases disproportionately with increasing load. (Requires additional tests.)

13.3. A subjective measure of the wear mechanisms present is often possible from a visual examination of the wear scar, with a distinct change in the surface topography after scuffing has been initiated. Scuffing is typically accompanied by a change in the sound of the test apparatus.

13.4. The scuffing load capacity is considered to be the minimum applied load at which scuffing *is* observed.

13.5. Scuffing onset is most easily defined through observation of the friction traces.

14. Report

14.1. Report the following information:

14.1.1. The applied load (not contact load) required to produce scuffing to the nearest 100 g.

14.1.2. Deviations from the standard conditions of the test load, relative humidity, and fuel temperature, etc.
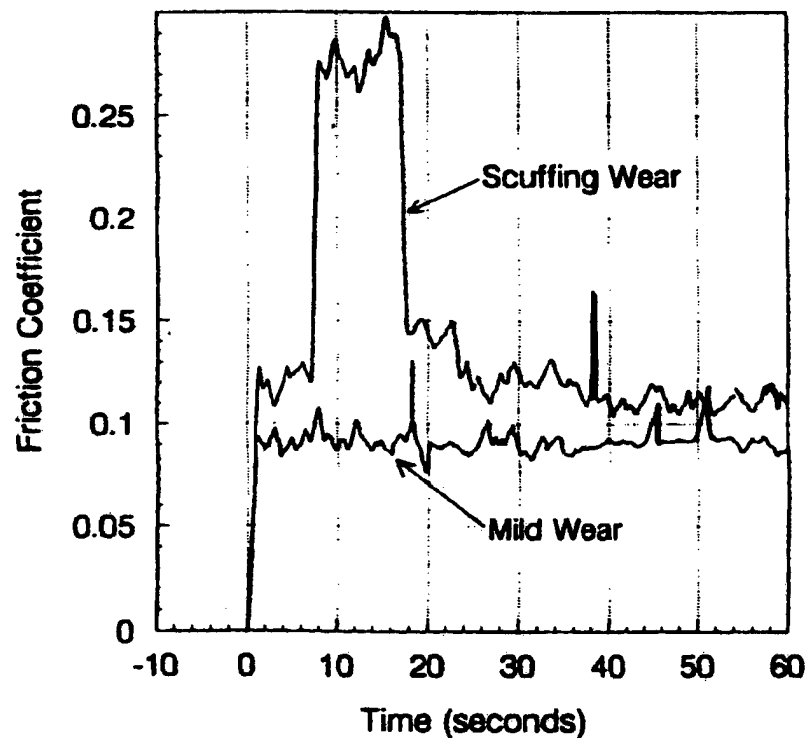
Figure B-1. Typical friction traces obtained during scuffing load wear tests

Suggested Test Load Sequence

START   RESULT

```
                                                                    900
                                                              1100
                                                    1300
                                             1400
                                                    1500
                                      1600
                                                    1700
                                             1800
                                                    1900
                               2000
                                                    2100
                                             2200
                                                    2300
                                      2400
                                                    2500
                                             2600
                                                    2700
          2800
                                                    2900
                                             3000
                                                    3100
                                      3200
                                                    3300
                                             3400
                                                    3500
                               3600
                                                    3700
                                             3800
                                                    3900
                                      4000
                                                    4100
                                             4200
                                                    4300
                                                              4500
                                                              4700
```
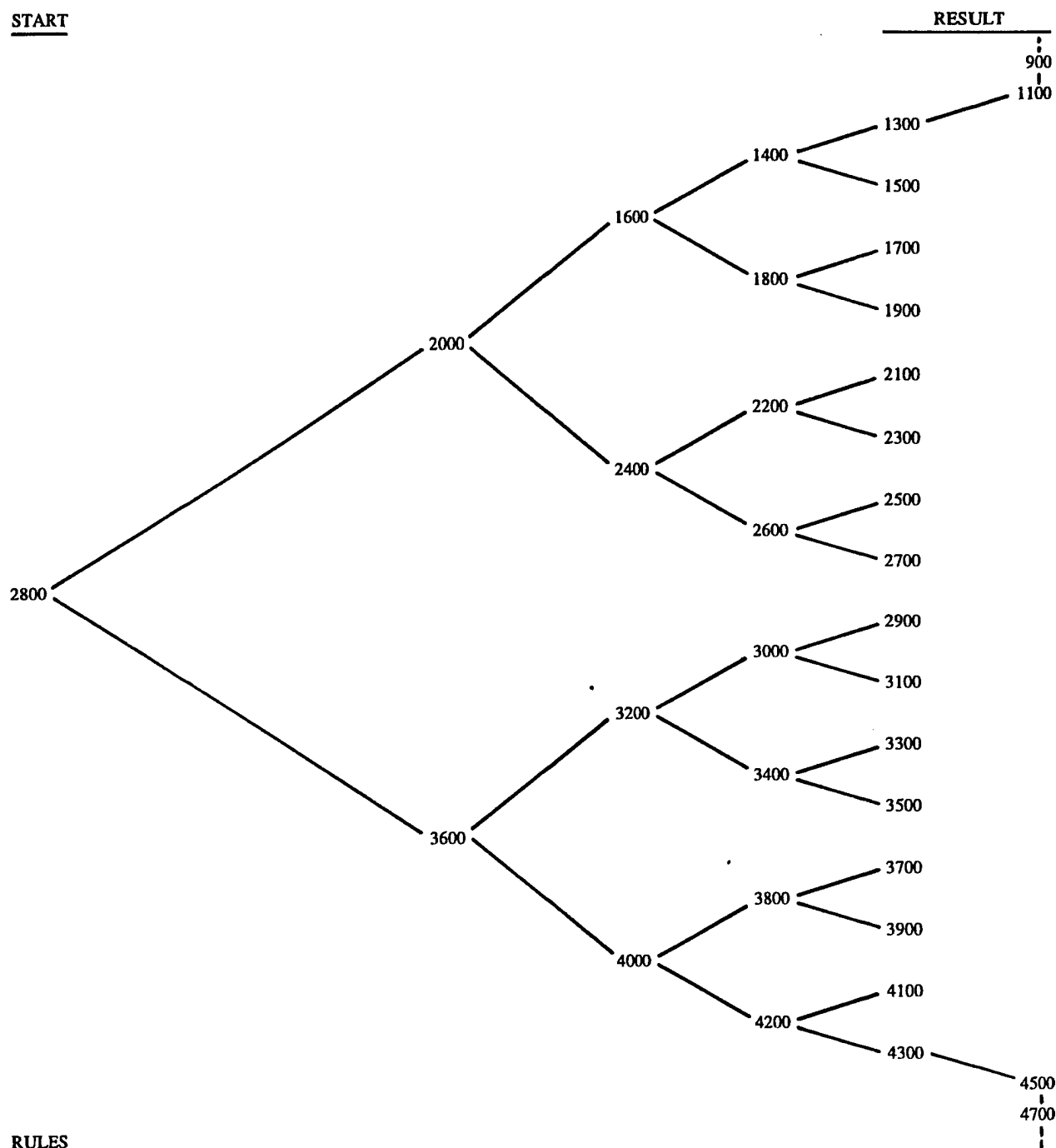
RULES

1. Move left to right when selecting load, start at 2,800 g.
2. If scuffing is observed, select the next lower load to the right (i.e., follow the upward arrow).
3. If no scuffing is observed, select the next higher load to the right (i.e., follow the downward arrow).
4. The result is the value obtained in the rightmost column to the nearest 200 g.
5. If necessary, additional tests may be performed to assess results outside the range 1,300 to 4,300 g. However, few fuels exceed the given range.

APPENDIX C

Test Procedure for the High Frequency Reciprocating Rig

Road Vehicles - Diesel Fuel - Performance Requirement and Test Method for Assessing Fuel Lubricity.

1 Scope

This International Standard specifies the performance requirement and test method for assessing the lubricating property of liquid fuels, specifically diesel fuel, including those which may contain a lubricity enhancing additive.

2 Field of Application

This International Standard applies to fuel used in diesel engines for road vehicles with fuel lubricated injection equipment at ratings less than 150 mm^3/stroke.

3 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ASTM D-329 Specification for Acetone

ASTM D-362 Specification for Industrial Grade Toluene

ASTM D-4306 Practice for Sampling Aviation Fuel for Tests Affected by Trace Contamination

AISI E-52100 Chromium Alloy Steel

ANSI B3.12. Metal Balls

ISO 6507-1:1982, Metallic materials - Hardness test - Vickers test - Part 1: HV 5 to HV 100.

4 Terminology

lubricity - a property of the fluid, measured by the wear scar, in millimeters, produced on an oscillating ball from contact with a stationary plate immersed in the fluid operating under closely controlled conditions.

5 Performance Requirement

The minimum performance requirement for diesel fuel in compliance with this standard shall be a Wear Scar Diameter (WSD) not greater than the following depending on test temperature:

Test Temperature	Maximum WSD
25° C	0.36
60° C	0.44

6 Summary of Test Method

The fluid under test is placed in a test reservoir in which the fluid temperature is maintained to the specified option. A fixed steel ball is held in a vertically mounted chuck and forced against a horizontally mounted stationary steel plate with an applied load. The test ball is oscillated at a fixed frequency and stroke length while being held fully immersed in the fluid reservoir. The metallurgies of the ball and plate, temperature, load frequency and stroke length are specified. The wear scar generated on the test ball is a measure of the fluid lubricating properties.

7 Significance and Use

Wear due to excessive friction resulting in shortened life of engine components such as diesel fuel injection pumps and injectors has sometimes been ascribed to lack of lubricity in the fuel.

The relationship of test results to diesel

injection system component distress due to wear has been demonstrated for some fuel/hardware combinations where boundary lubrication is a factor in the operation of the component.

The wear scar generated in the test method specified herein, is sensitive to contamination of the fluids and test materials and the temperature of the test. Lubricity measurements are also sensitive to trace materials acquired during sampling and storage. Containers specified in Practice ASTM D-4306 shall be used.

8 Apparatus

The test apparatus shall be capable of engaging a steel ball loaded against a stationary steel plate with an applied load and oscillating at a fixed frequency and stroke length while being held fully immersed in a fluid reservoir according to the test conditions in table 1.

Table 1 - Test Conditions

Fluid Volume	1 ± 0,20 ml
Stroke Length	1 ± 0,02 mm
Frequency	50 ± 1 Hz
Fluid Temperature	25 ± 1° C or 60 ± 1° C
Applied Load	200 g
Test Duration	75 ± 0,1 min
Bath Surface Area	6 ± 1 cm^2
Fluid Volume	1 ± 0,20 ml

Specimen Bath, capable of holding a specimen plate in a rigid manner and which will also contain the test fuel. The temperature of this bath, and consequently the test fuel contained in it, should be achieved by means of an electrically controlled heater pad to which the specimen bath can be closely attached.

Control Unit, for controlling variable parameters.

An electronic data acquisition and control system.

Microscope, capable of 100 x magnification in graduations of 0,1 mm and incremented in divisions of 0,01 mm.

Glass Slide Micrometer, with a scale ruled in 0,01 mm divisions.

Cleaning Bath - Ultrasonic seamless stainless steel tank with a capacity of 1.9 L and a cleaning power of 40 W.

9 Reagents and Materials

Test Plate, of AISI E-52100 steel machined from annealed rod. having a Vickers hardness "HV 30" scale number of 190 - 210, turned, lapped, and polished to a surface finish of less than 0,02 μm root mean square.

Test Ball, of AISI E-52100 steel, with a diameter of 6,00 mm, having a Rockwell hardness "C" scale (HRC) number of 58 - 66, and a surface finish of less than 0,05 μm root mean square.

Compressed Air, (Warning - See Note 1), containing less than 0,1 ppm hydrocarbons and 50 ppm water.

> Note 1:Warning-Compressed gas under high pressure. Use with extreme caution in the presence of combustible material, since the autoignition temperatures of most organic compounds in air are drastically reduced at elevated pressures. See Annex A.1.

Desiccator, containing a non-indicating drying agent, capable of storing test plates. balls, and hardware.

Gloves, clean, lint-free, cotton, disposable.

Wiper, wiping tissue. light duty, lint free. hydrocarbon free. disposable.

Toluene. (Warning - see Note 2), conforming to ASTM D-362.

Note 2: Warning - Flammable. Harmful if inhaled. See Annex A.2.

Acetone, (Warning - see Note 3), conforming to ASTM D-329.

Note 3: Warning - Extremely flammable. Vapors may cause flash fire. See Annex A.3.

Reference Fluid, (Warning - see Note 4), shall be a narrow-cut isoparaffinic solvent (ISOPAR M, manufactured by the Exxon Company).

Note 4: Warning - Flammable. Vapor harmful. See Annex A.4.

10 Preparation of Apparatus

Test Plates, as received:

The test plates shall be partially stripped of any wax-like protective coatings by manually rubbing them with rags or paper towels saturated with toluene. Place partially cleaned plates in a clean beaker. Transfer a sufficient volume of toluene in the beaker such that the test plates are completely covered. Place beaker in ultrasonic cleaner and turn on for 7 minutes. Remove the test plates and repeat the above procedure except with acetone for 2 minutes. Dry. Rinse with acetone. Dry and store in desiccator. Handle all clean test pieces with clean forceps or disposable gloves.

Note 5: Drying operations can be accomplished using compressed air jet at 140 - 210 kPa pressure.

Test Balls, as received:

The test balls are to be cleaned following the same procedure as for the test plates.

Hardware:

The hardware, fixtures, fittings, and utensils, that is all items that come into contact with the test plates, test balls, or test fuel, shall be cleaned by washing thoroughly with toluene, dried, and rinsed with acetone. Dry and store in a desiccator.

11 Calibration and Standardization

The temperature control of the lower specimen bath should be checked using a calibrated temperature measuring device.

The frequency of the vibrator unit should be checked with a calibrated frequency meter.

The stroke length should be checked by measuring the wear scar on the lower specimen, using a calibrated microscope, after running a test on the reference fluid. The width of the wear scar should be subtracted from the length of the wear scar to give the actual stroke length.

The run time should be checked with a calibrated stopwatch.

The test rig shall be calibrated by testing the reference fluid in accordance with Section 12. Perform two tests at the test temperature to which the test rig is being calibrated. Further tests or corrective action to further calibrate the test rig will be required if the WSD's differ more than 0,04 mm at 25° C and 0,06 at 60° C from each other or from the average WSD for the reference fluid which at 25° C is 0,582 mm and at 60° C is 0,625 mm.

12 Procedure

The greatest care shall be taken to adhere strictly to cleanliness requirements and to the specified cleaning procedures. During handling and installation procedures. protest

cleaned test parts (plates, balls, reservoir, and fixtures) from contamination by wearing clean cotton gloves.

Using forceps, place the lower specimen (test plate) into the specimen bath, shiny side up. Secure the test plate to the bath and the bath to the test rig. Assure the thermocouple is properly placed in the reservoir.

Using forceps, place the test ball into the holder and attach the holder to the end of the vibrator arm. Ensure the holder is horizontal before fully securing the unit.

Using a pipette, place 1 mL of the test fuel into the bath.

Set the temperature controller to the desired test temperature and switch on the heater. Set the stroke length. Set the vibration frequency.

When the temperature has stabilized, lower the vibrator arm and suspend a 200 g weight from the arms. Start the vibrator unit.

Operate the test for 75 minutes. At the completion of the test, switch off the vibrator unit and the heater. Lift up the vibrator arm and remove the upper specimen holder.

Rinse the upper specimen (still in the holder) in cleaning solvents and dry with a tissue. Using a permanent marker, circle the wear scar on the ball.

Remove the lower specimen bath, properly dispose of the fuel. Remove the disc and wipe it clean. Place the disc in a storage receptacle (plastic bag) marked with the unique test reference.

Place the upper specimen holder under the microscope and measure the wear scar diameter per clause 13.

Upon completion of the wear scar measurement, remove the upper specimen form the holder and place the ball together in

storage with the lower specimen.

13 Measure of the Wear Scar

Turn on microscope light and position test ball under microscope at 100 x magnification.

Focus microscope and adjust stage such that wear scar is centered within the field of view.

Align the wear scar to a divisional point if reference on the numerical scale with the mechanical stage controls. Measure the major axis to the nearest 0.01 mm. Record the readings on the data sheet.

Record condition of wear area if different from the reference standard test, that is, debris color, unusual particles or wear pattern, visible galling, etc., and presence of particles in the reservoir.

14 Calculation

Calculate the wear scar diameter as follows:

$$WSD = (M + N)/2$$

where:

WSD = wear scar diameter, mm,
M = major axis, mm, and
N = minor axis, mm.

15 Report

Report the following information:
Wear scar diameter to the nearest 0.01 mm,
Description of the wear scar area,
Fuel temperature,
Description of the test fuel,
Identification of test specimens, and
Date.

16 Precision and Bias

Precision - The precision was developed for fuels with a wear scar diameter between 0.15

and 0,70 mm. The precision of this test method determined by the statistical examination of inter-laboratory test results according to ISO 4259 is as follows:

Repeatability - The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values in only one case in twenty:

repeatability:
$$@ 60° C = 0,075$$
$$@ 25° C = 0,104$$

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values in only one case in twenty:

reproducibility:
$$@ 60° C = 0,130$$
$$@ 25° C = 0,166$$

Bias - The procedure in this test method has no bias because the value of lubricity can be defined only in terms of a test method.

ANNEX

(Mandatory Information)

PRECAUTIONARY STATEMENTS

A.1 Compressed Air (Cylinder)

Keep cylinder valve closed when not in use.
Always use a pressure regulator. Release
regulator tension before opening cylinder.
Do not transfer to cylinder other than one in
which air is received. Do not mix gases in
cylinder.
Do not drop cylinder. Make sure cylinder is
supported at all times.
Stand away from cylinder outlet when opening
cylinder valve.
Keep cylinder out of sun and away from heat.
Keep cylinders form corrosive environment.
Do not use cylinder without label.
Do not use dented or damaged cylinders.
For technical use only. Do not use for
inhalation purposes.

A.2 Toluene

Keep away from heat sparks, and open flame.
Keep container closed.
Use with adequate ventilation.

Avoid prolonged breathing of vapor or spray
mist.
Avoid contact with eyes and skin.

A.3 Acetone

Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid build-up of vapors, and eliminate all
sources of ignition, especially nonexplosion-
proof electrical apparatus and heaters.
Avoid prolonged breathing of vapor or spray
mist.
Avoid contact with eyes or skin.

A.4 Isoparaffinic Solvent

Keep away from heat, sparks, and open flame.
Keep container closed.
Use with adequate ventilation.
Avoid breathing vapor or spray mist.
Avoid prolonged or repeated contact with skin.

APPENDIX D

Description of Aquatest IV Apparatus

Operating Instructions Aquatest IV

9928124

TABLE OF CONTENTS

Operating Instructions Aquatest IV

1. INTRODUCTION

The AQUATEST IV is an automatic analyzer for the determination of water. It is the most advanced version of Photovolt's coulometric titrators and incorporates microprocessor control. It is based on the specific and quantitative reaction of water with Karl Fischer reagent. This instrument is unique in that the reagent is generated electrolytically rather than added from a burette. This eliminates the need for standardization or calibration because 1 coulomb is equivalent to 186.53 micrograms of water.

The simplest mode of operation of the AQUATEST IV consists of three steps: 1) depress the $\boxed{\text{START}}$ key; 2) introduce the sample; and 3) wait until the result is displayed. To obtain the result in percent or parts per million, to automatically correct for a solvent blank of diluted or extracted samples, etc. is equally straightforward and requires a few additional key strokes. The exact procedures are tabulated in Section 4 and the same information is shown in flowchart form in Section 5 for quick reference.

2. DESCRIPTION OF THE INSTRUMENT

The base of the AQUATEST IV encloses the electronics and the magnetic stirrer. The on-off switch is at the lower left side. All other controls are actuated by the keyboard as described in Section 3.1. The display shows the analytical results as well as instructions and warning signals (see Section 3.2). To the right of the display is a post onto which the titration vessel is clamped. This post also carries the polarized power connections to provide the direct current required for electrolysis (generation of iodine), and polarized connections for the sensing electrode, which monitors the water content.

The titration vessel holds the vessel solution and a magnetic stirring bar. The cover is clamped onto the ground glass lip of the vessel. This cover has a sample port, an air vent, a sensing electrode and a generator assembly.

The generator assembly has an outer platinum mesh anode, a Pyrex glass frit to separate the vessel solution (anolyte) from the generator solution (catholyte) and an inner platinum mesh cathode. The generator solution is poured into the top of the assembly and then a loose-fitting cap is placed on the generator as a shield. The pinhole in the cap prevents development of a pressure differential.

The electrolysis current is 100.35mA stabilized to ± 0.1%. There is also a current of −25.09mA for reverse electrolysis. After the titration is started and the sample is introduced, the current will flow until the equivalence point is reached. A preliminary figure is displayed without units. Subsequently, the inherent "drift" of the system is determined within approximately a minute and the preliminary value corrected. This final value is displayed with the mcg, ppm or pcr symbol. A detailed description of the method is found in Section 9.
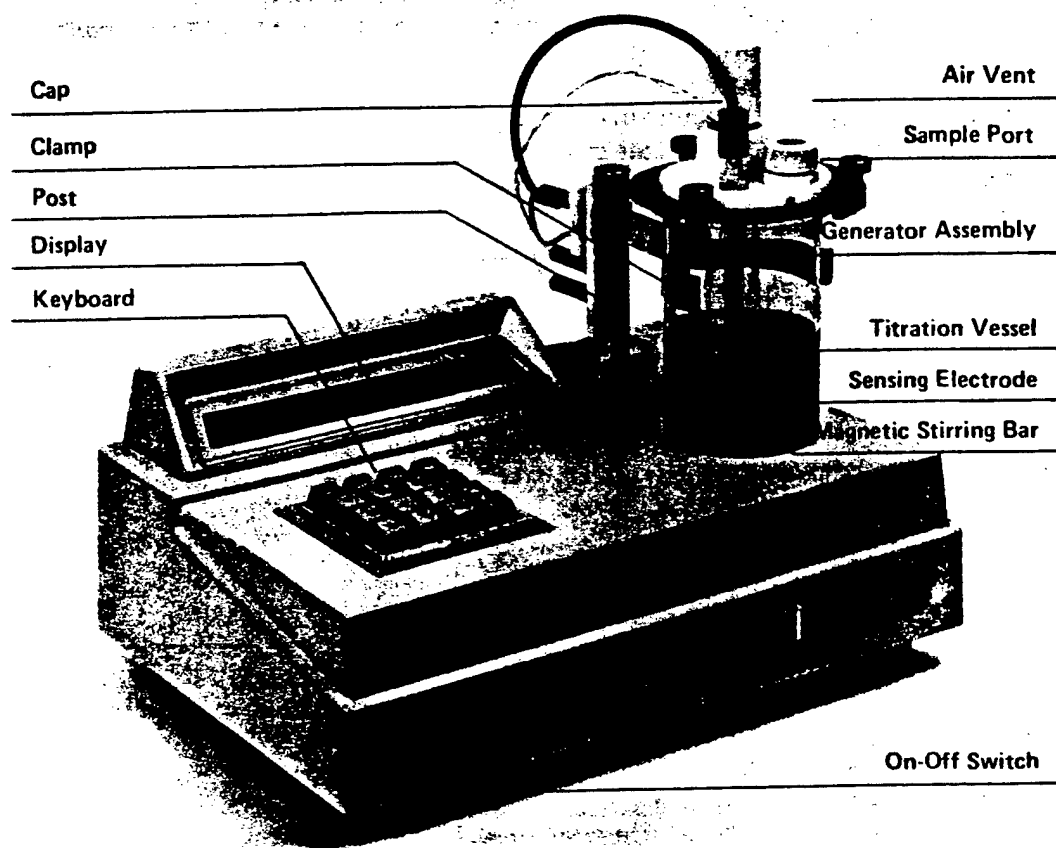
Figure 1. THE AQUATEST IV

3. DESCRIPTION OF CONTROLS

3.1 Keyboard

(a) The numbers, decimal point, CLEAR , and ENTER keys serve to enter and clear numerical data. These data are the sample weight in milligrams (prompted by the display *mg*); blank value in micrograms (prompted by display *-mcg*); extraction delay time in minutes (prompted by the display *m·n*); and sample identification number for an external printer (prompted by the display *·d*).

(b) ENTER is also used to select the following functions:

(1) ENTER + 0 allows storage of a blank which is subtracted from the titration result.

→(2) ENTER + 1 allows storage of an extraction delay time. (This entry also erases the previous result in anticipation of the next analysis.)

(3) ENTER + 2 acts as a switch to the stirrer. Consecutive ENTER + 2 actions stop and start the stirrer.

(4) ENTER + 3 permits the entry of a 4-digit sample identification number to an external printer. A 2-digit number which serializes the number of replicates of the sample is appended automatically.

(c) %/ppm sets the AQUATEST IV into the percent mode. The display will prompt entry of the sample weight in milligrams. The final answer is given in parts per million up to 1280 and in percent from 0.128% upwards.

(d) mcg is used to reset the display to the microgram mode.

(e) START serves to initiate the analysis. The START key is active only when *mcg, ppm* or *pct* appears in the right side of the display. During the titration, the entire keyboard, including the START key, is disabled.

3.2 Display

(a) The left side of the display shows: 1) results up to 5 digits; 2) data entries prior to their transfer to memory by the [ENTER] key; and 3) *Error*, which, in conjunction with indications (11) and (12) below, pinpoints an instrument malfunction.

(b) The right side of the display shows:

(1)	*mcg*	micrograms of water titrated
(2)	*mg*	milligrams of sample weight
(3)	*ppm*	parts per million of water content (up to 1280)
(4)	*pct*	percent moisture from 0.128% to 100%
(5)	*_mcg*	blank value in micrograms subtracted from the result
(6)	....	result includes blank correction
(7)	*m.n*	extraction delay time in minutes
(8)	*Str*	extraction delay stirring in operation
(9)	*WAIT*	titration chamber not yet at equivalence point ([START] key is inoperative)
(10)	*SMPL*	sample is to be introduced (within 7 seconds)
(11)	*ELEC*	indicates that the sensing electrode circuit is open
(12)	*Soln*	indicates that the system has excessive electrical resistance (see Section 8)
(13)	*id*	sample identification number (for external printer) .

3.3 Power Switch

To the left on the base of the instrument is a slide switch. It is the power switch. It should be left on at all times, except when the AQUATEST IV is moved or, perhaps, if it is not to be used for long periods of time.

{ CAUTION }

When power is shut off, all data are removed from memory and must be re-entered when the AQUATEST IV is subsequently powered up. At that time the AQUATEST IV is in the microgram mode. Any entry, according to Sections 4.2, 4.3, 4.4 or 4.6, whichever is applicable, has to be repeated.

---

4. OPERATION

4.1 For Microgram Mode

	DEPRESS	DISPLAY	COMMENTS
4.1.1	[START]	*SMPL*	When *SMPL* is displayed, introduce the sample immediately; titration begins automatically after a 7-second delay. If *WAIT* appears before *SMPL*, the instrument is not at equivalence; inject the sample when *SMPL* comes on.
4.1.2		XXXXX	After the titration, the uncorrected answer is held about one minute.
4.1.3		XXXXX *mcg*	The corrected result in micrograms of water is displayed. To return to the percent mode, depress [%/ppm] and [ENTER] . If additional samples are to be analyzed, all of which have the same sample weight, begin directly with step 4.2.3 below.

4.2 For Percent Mode

For repetitive analyses with the same sample weight, begin with step 4.2.3.

	DEPRESS	DISPLAY	COMMENTS
4.2.1	%/ppm	XXXXX mg	If the number in the display is not the correct sample weight, depress CLEAR . Use the keyboard to enter the sample weight in milligrams.
4.2.2	ENTER	XXXXX ppm, or XXXXX pct	The sample weight is entered into memory. The number displayed reflects the computation based on the previous titration.
4.2.3	START	SMPL	When SMPL is displayed, introduce the sample immediately; titration begins automatically after a 7-second delay. If WAIT appears before SMPL, the instrument is not at equivalence; inject the sample when SMPL comes on.
4.2.4		XXXXX	After the titration, the uncorrected answer is held about one minute.
4.2.5		XXXXX ppm, or XXXXX pct	The corrected answer will be in parts per million (up to 1280) or in percent (from 0.128%). Note: above 8.129%, the display will show two decimal places (e.g. 8.193% will be displayed as 8.19 pct). To display the answer in micrograms, depress mcg

4.3 With Solvent Blank

If the sample is dissolved in a solvent, the water content of the solvent should be measured as a separate sample and entered into the memory. This blank is then subtracted from the water content of the dissolved sample; the answer displayed is thus the water content of the original sample alone. If the same quantity of the same solvent is used in repetitive analyses, and if the solvent blank has been entered previously, proceed to START according to either 4.1.1 or 4.2.3.

	DEPRESS	DISPLAY	COMMENTS
4.3.1	ENTER + 0	XXXXX -mcg	If the solvent blank in the display is not correct or if the blank is not required, depress CLEAR . Enter the correct solvent blank.
4.3.2	ENTER	XXXXX mcg, or XXXXX ppm/pct	The blank value is stored in memory and the instrument is ready. Note: the final answer will appear with mcg, ppm, or pct.

4.4 With Pretitration Stirring

When solids or oils are analyzed and an extraction period is required, the AQUATEST IV can be programed to do this automatically. For repetitive analyses with the same extraction time, begin with step 4.4.3. Note: step 4.4.1 will clear the previous result.

	DEPRESS	DISPLAY	COMMENTS
4.4.1	[ENTER] + [1]	XXX.XX $m \cdot n$	If the number in the display is not correct (or if extraction is not desired) depress [CLEAR] Use the keyboard to enter an extraction time in minutes (up to two decimal places).
4.4.2	[ENTER]	0 mcg, or 0 $ppm/pc\tau$	The extraction time is stored in memory and the instrument is ready.
4.4.3	[START]	$S\Pi PL$	Introduce the sample immediately after $S\Pi PL$ is displayed. After 7 seconds the display will show $S\tau \cdot r$ for the programed period; the titration will then proceed automatically.

4.5 Stirrer Switch

	DEPRESS	DISPLAY	COMMENTS
4.5.1	[ENTER] + [2]		Stirrer stops
4.5.2	[ENTER] + [2]		Stirrer restarts

4.6 For Sample Identification
(with Printer)

If the AQUATEST IV is connected to a printer (or to some other EIA RS232c 300 baud compatible device), a sample identification number entered will be transmitted following the result of the analysis. In addition, a 2-digit serialization will be appended with each analysis. The connector for the printer is at the rear of the instrument.

	DEPRESS	DISPLAY	COMMENTS
4.6.1	[ENTER] + [3]	XXXX $\cdot d$	If the identification number is incorrect, depress [CLEAR] . Use the keyboard to enter the identification number (up to 4 digits). This step resets the serialization to zero.
4.6.2	[ENTER]	(Temporarily blank during printing.)	The identification number is stored in memory and the instrument is ready.

```
┌─────────────────────────────────────────────────────────────┐
│                    ┌──────────────┐                          │
│                    │     NOTE     │                          │
│                    └──────────────┘                          │
│  If the sample is introduced beyond the 7 second limit, the AQUATEST IV │
│  will titrate essentially zero and lock in. The late sample itself will not be │
│  titrated but treated as extraneous moisture and if START is depressed during │
│  this time period,  WR IT  will be displayed until the system recovers. │
└─────────────────────────────────────────────────────────────┘
```

5. AQUATEST OPERATIONS IN FLOWCHART FORM

The flowcharts pose questions in the diamond-shaped decision blocks. In each case there is a "YES" and "NO" answer. Follow the appropriate arrow, and it will lead to actions described in the rectangular boxes until the completion of the analysis.

By way of example, suppose the AQUATEST IV is to be operated in the microgram mode, but the display shows 2.31 pct. See chart 5.1; the first answer is "NO" and the second is "YES", leading to the instructions "Depress mcg" and "Depress START; add sample".

5.1 Microgram Mode

```
  ┌─────────┐        ┌─────────┐        ┌─────────┐        ┌─────────┐
 ╱ DISPLAYS ╲  NO   ╱ DISPLAYS ╲  NO   ╱  RIGHT   ╲  NO   ╱  DIS-    ╲  NO   ┌──────────────┐
╱  ˈ mcg ?   ╲────▶ ╱ ppm OR   ╲────▶ ╱ SIDE OF   ╲────▶ ╱ PLAYS mg  ╲────▶ │   REMEDY     │
╲            ╱      ╲ pcᴛ ?    ╱      ╲ DISPLAY   ╱      ╲ ˍmcg ˌd   ╱       │   Error      │
 ╲         ╱         ╲       ╱         ╲ BLANK?  ╱         ╲ mˌn ?  ╱        │  DISPLAYED.  │
  └───┬───┘           └───┬──┘          └───┬──┘            └──┬──┘          └──────────────┘
      │ YES               │ YES             │ YES              │ YES
      ▼                   ▼                 ▼                  ▼
┌─────────────┐     ┌──────────┐     ┌──────────┐      ┌─────────────┐
│ DEPRESS     │     │ DEPRESS  │     │ WAIT UNTIL│     │ DEPRESS CLEAR│
│ START :     │◀────│  mcg  .  │◀────│ END OF TI-│     │ AND/OR ENTER │
│ ADD SAMPLE. │     └──────────┘     │ TRATION.  │     └─────────────┘
└──────┬──────┘                      └──────────┘
       │
       ▼
┌─────────────┐
│ WAIT FOR mcg│
│ TO APPEAR AT│
│ RIGHT OF DISPLAY.*│
└─────────────┘
```

5.2 Percent Mode

```
  ┌─────────┐        ┌─────────┐        ┌─────────┐        ┌─────────┐
 ╱ DISPLAYS ╲  NO   ╱ DISPLAYS ╲  NO   ╱  RIGHT   ╲  NO   ╱  DIS-    ╲  NO   ┌──────────────┐
╱  ppm OR    ╲────▶ ╱  mcg ?   ╲────▶ ╱ SIDE OF   ╲────▶ ╱ PLAYS mg, ╲────▶ │   REMEDY     │
╲  pcᴛ ?     ╱      ╲          ╱      ╲ DISPLAY   ╱      ╲ ˍmcg ˌd   ╱       │   Error      │
 ╲         ╱         ╲       ╱         ╲ BLANK?  ╱         ╲ mˌn ?  ╱        │  DISPLAYED.  │
  └───┬───┘           └───┬──┘          └───┬──┘            └──┬──┘          └──────────────┘
      │ YES               │ YES             │ YES              │ YES
      │                   │                 ▼                  ▼
      │                   │          ┌──────────┐      ┌─────────────┐
      │                   │          │ WAIT UNTIL│     │ DEPRESS CLEAR│
      │                   │          │ END OF TI-│     │ AND/OR ENTER .│
      │                   │          │ TRATION.  │     └─────────────┘
      ▼                   │          └──────────┘
 ┌─────────┐              │
╱ REPEAT    ╲  NO   ┌──────────────────────────────┐
╱ ANALYSIS-  ╲────▶ │ DEPRESS %/ppm + CLEAR ;      │
╲ SAMPLE WT. ╱      │ ENTER SAMPLE WEIGHT (mg).    │
 ╲ SAME?   ╱        │ DEPRESS ENTER .              │
  └───┬───┘         └──────────────────────────────┘
      │ YES
      ▼
┌─────────────┐
│ DEPRESS     │
│ START ;     │
│ ADD SAMPLE. │
└──────┬──────┘
       │
       ▼
┌──────────────────┐
│ WAIT FOR mcg, ppm,│
│ OR pcᴛ TO APPEAR AT│
│ RIGHT OF DISPLAY.*│
└──────────────────┘
```

*The final result will be in memory and can be retrieved until the next sampling cycle is initiated by depressing START or ENTER + I (extraction delay time).

D-11

5.3 Analysis with Blank Correction

```
            REPEAT
          ANALYSIS —        NO
          SAME BLANK   ──────────►   DEPRESS ENTER + 0 .
          CORRECTION
             ?
             │
             │ YES                          │
             │                              ▼
             │                          CORRECT        NO
             │                          BLANK IN  ──────────►   DEPRESS CLEAR ; ENTER
             │                          _ mcg                   PROPER BLANK IN _ mcg.
             │                            ?
             │                            │
             │                            │ YES
             ▼                            ▼
      DEPRESS START :   ◄────────   DEPRESS ENTER .   ◄──────────────
         ADD SAMPLE.
             │
             ▼
      WAIT FOR mcg, ppm.
      OR pct TO APPEAR AT
      RIGHT OF DISPLAY.
```
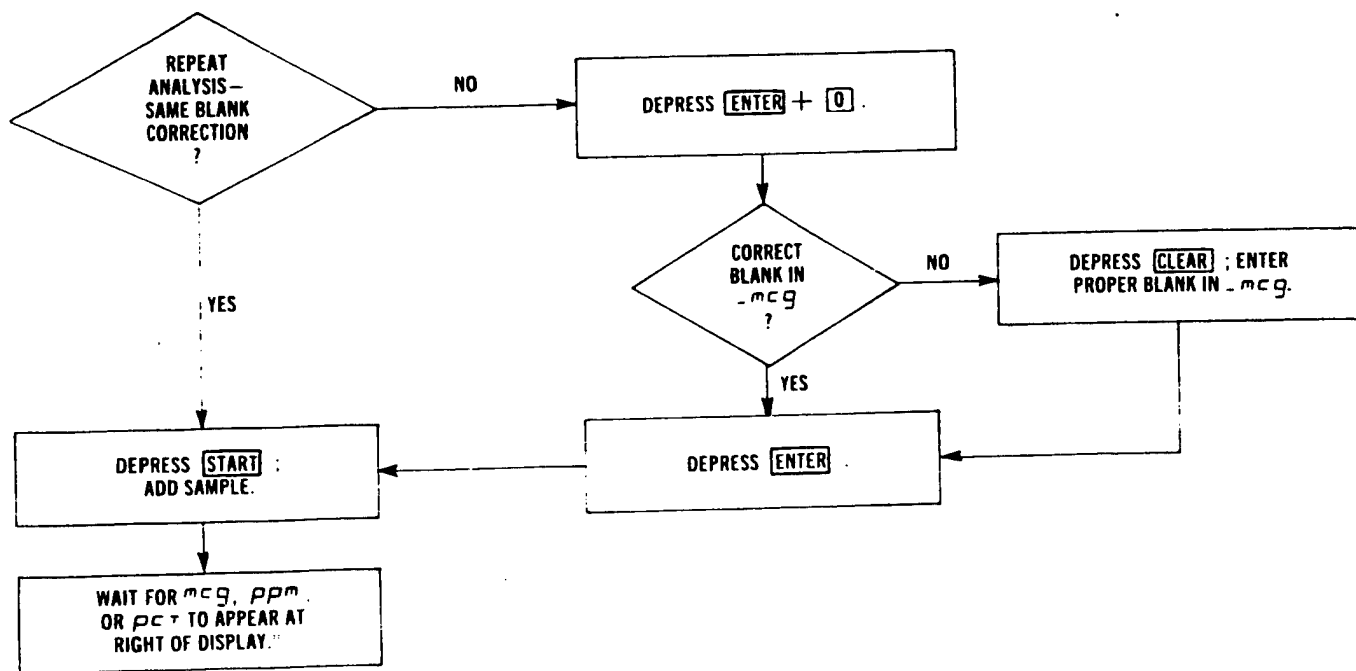
5.4 Analysis with Pre-Extraction
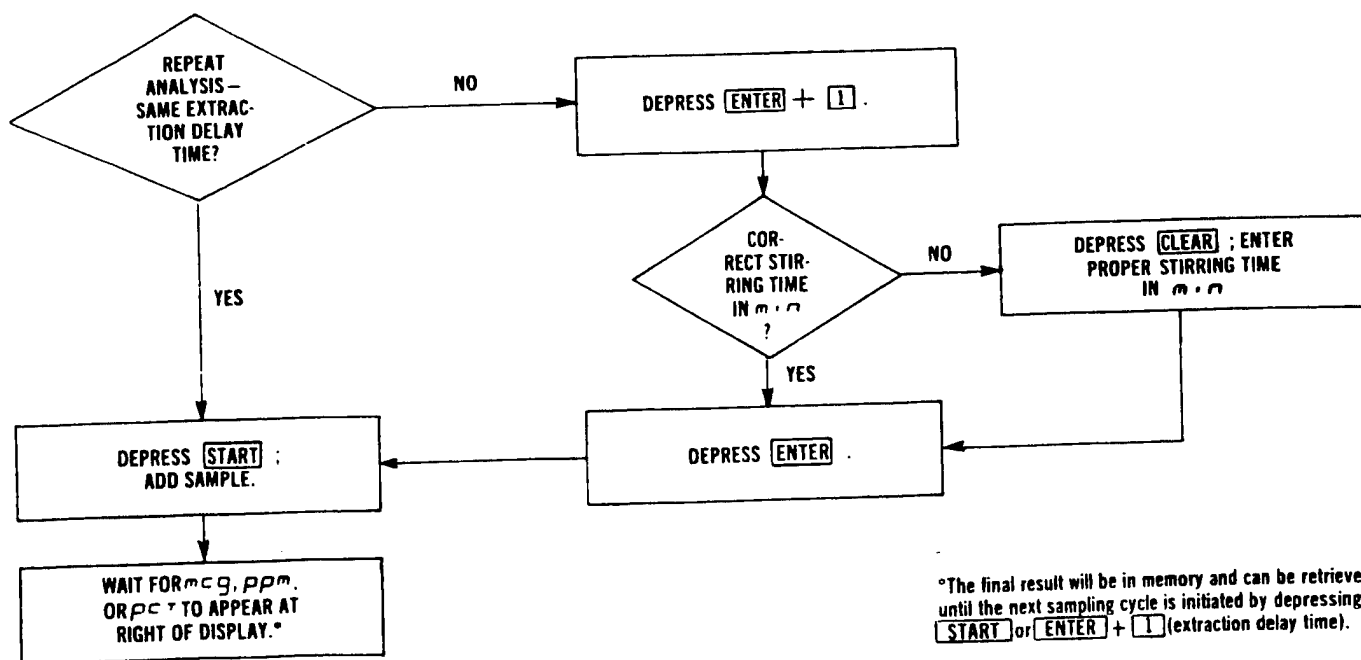
```
            REPEAT
          ANALYSIS —         NO
          SAME EXTRAC-  ──────────►   DEPRESS ENTER + 1 .
          TION DELAY
            TIME?
             │                              │
             │                              ▼
             │                          COR-
             │                          RECT STIR-      NO
             │                          RING TIME  ──────────►   DEPRESS CLEAR ; ENTER
             │                          IN min                   PROPER STIRRING TIME
             │ YES                        ?                      IN min
             │                            │
             │                            │ YES
             ▼                            ▼
      DEPRESS START :   ◄────────   DEPRESS ENTER .   ◄──────────────
         ADD SAMPLE.
             │
             ▼
      WAIT FOR mcg, ppm.
      OR pct TO APPEAR AT
      RIGHT OF DISPLAY.*
```

*The final result will be in memory and can be retrieved until the next sampling cycle is initiated by depressing START or ENTER + 1 (extraction delay time).

6. SETTING UP THE INSTRUMENT

Remove the small cartons from the package containing the Aquatest IV. Then lift out the Aquatest IV. Identify all parts on the packing list. Report any broken or missing parts. If all is in good order, return the warranty card.

Prepare the chemicals by pouring the contents of one bottle of vessel solution part "B" into one bottle of vessel solution part "A". Close the bottle, invert a few times, and allow to cool to room temperature for one-half hour.

Set up the Aquatest IV in an area away from direct sunlight and radiators. Determine that a grounded AC receptacle is available. Check the voltage on the nameplate on the rear of the instrument.

Install the Generator Assembly into the cover of the Titration Vessel. Invert the cover and pass the cables through the large threaded hole. Handle the generator assembly only by the teflon collar. Turn the assembly until the flange is seated securely against the underside of the lid.

Snap the titration vessel into the clamp. Lightly grease the ground glass flange using the special sealing grease supplied.

Place the teflon-coated stirring bar in the vessel. Place the cover and ring assembly on top of the vessel. Make certain that the three tabs clear the flange of the vessel. Fasten the cover by flipping the tabs inward and then tighten the three thumb screws (See Figure 2). Lightly grease the taper of the sensing electrode and insert it into the cover in the orientation shown in Figure 3 with the loop towards the outside and parallel. Pour in the prepared vessel solution using the funnel supplied. Open a vial of generator solution, pour the contents into the generator and close with the cap, which has a pinhole in it. Now swirl the vessel to dry the air space above the vessel solution.
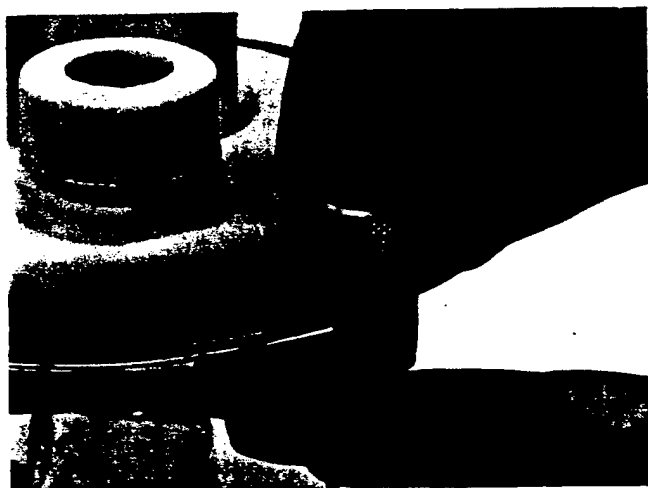
Figure 2. THUMBSCREWS
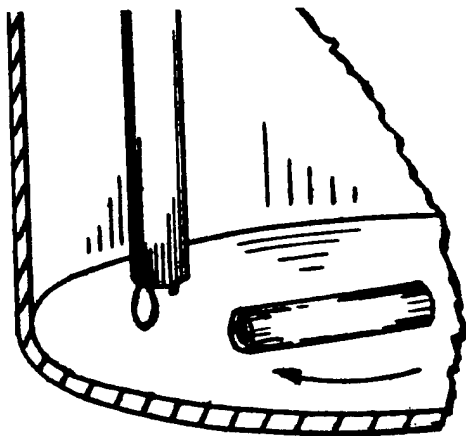
Figure 3. SENSING ELECTRODE
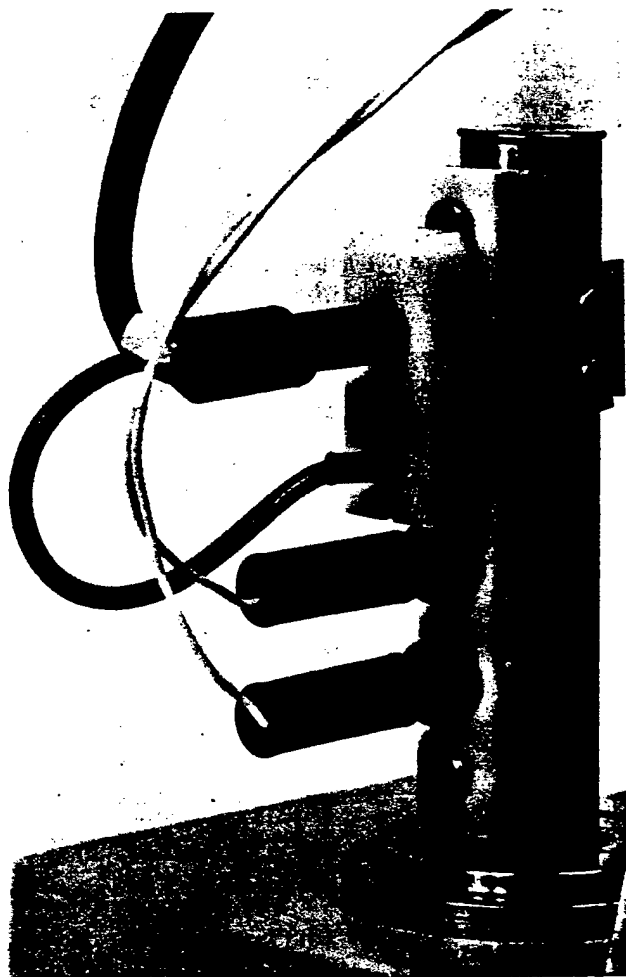
Figure 4. CONNECTORS

Plug the two banana plugs from the generator into the two lower jacks of the post, black to black and red to red for proper polarity; then plug the sensing electrode into the upper two jacks. (See Figure 4.)

Plug the power cable of the AQUATEST IV into a 110V AC receptacle. (A 220 V version is supplied under Cat. No. 02-124-20 and is to be connected to a 220V AC outlet.)

Switch on the power if not already on; the AQUATEST IV will display the indication $WA \cdot IT$. Affix the 4½-inch needle to the plastic syringe. Draw approximately 10 ml of neutralizing solution into the syringe, insert the needle through the rubber membrane and slowly add the solution. The total volume required will range between 5 and 15 ml. As the color of the vessel solution becomes lighter and the stirring bar becomes visible, make the addition *very slowly*. The endpoint is reached when the solution turns amber-colored and the display of the AQUATEST IV changes from $WA \cdot IT$ to $0mcg$. Depress START to verify that the instrument is ready. If $SMPL$ appears, the instrument is ready. If an excess of neutralizing solution has been added, $WA \cdot IT$ will appear instead of $SMPL$. When the water in the excess neutralizing solution has been titrated, $0mcg$ will be displayed automatically. This may take a long time depending on the amount of excess.

7. SAMPLING

7.1 Sample Size
The desirable sample size contains between 100 and 3000 micrograms of water. The least detectable amount is about 10 micrograms; however, reliable analysis requires a larger sample. The following table is a guide for appropriate sample size.

Expected Moisture Content	Range of Sample Size
10 ppm	10 g or more
100 ppm	1 - 30 g
1000 ppm (0.1%)	0.1 - 3 g
1%	10 - 300 mg
10%	1 - 30 mg
100%	0.1 - 3 mg

Samples containing 10% or more water may require a sample size so small that it is hard to manage. In such instances, it is recommended to dilute the sample rather than dump large amounts of wet sample into the titration vessel. The reason is two-fold; first, the titration itself will require a very long time and, second, the wet sample will contaminate the system.

The dilution technique is simple. Measure a suitable sample volume, say 1 ml, into a serum vial or small bottle; add a measured volume, e.g. 9 ml, of a solvent such as methyl alcohol, and mix well. Then run a titration of 1 ml of the solvent and enter the result as a blank into the AQUATEST IV. Now titrate 1 ml of diluted sample and the result multiplied by 10 is the final answer.
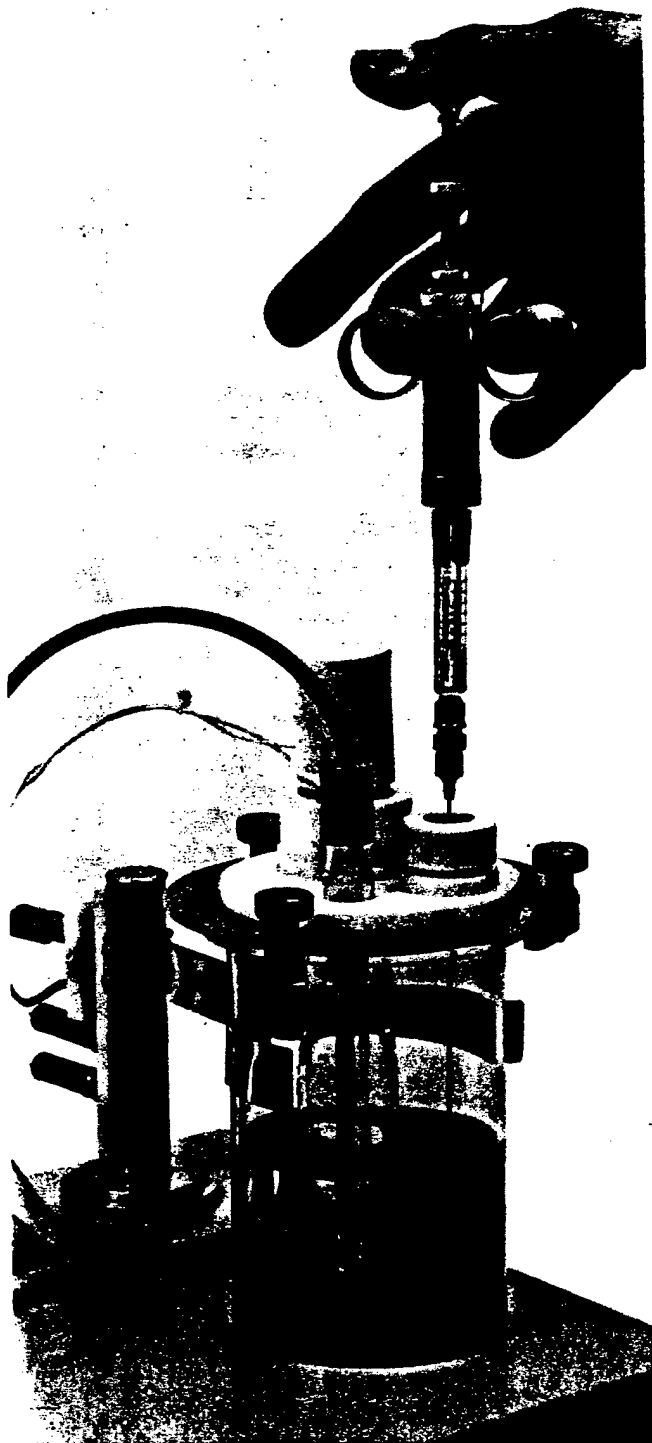
Figure 5. TRANSFER OF LIQUIDS

Figure 6. TRANSFER OF SOLIDS
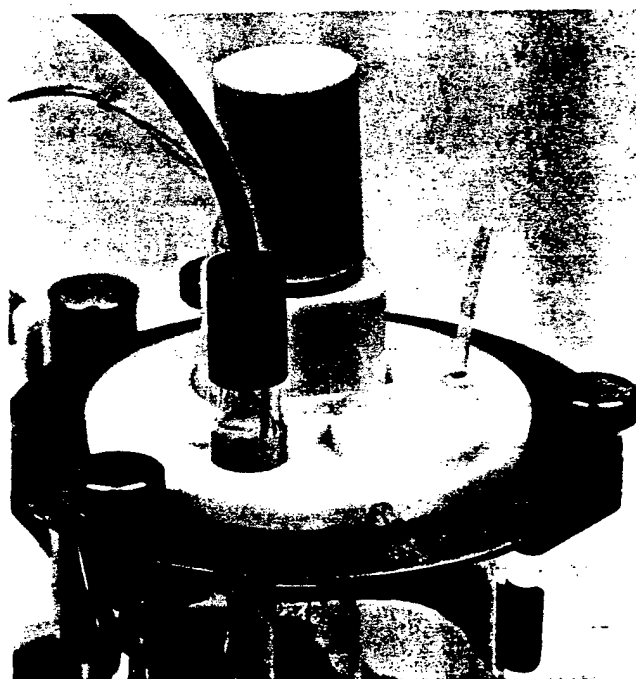
Figure 7. TEFLON PLUG

7.2 Transfer of Liquid Samples

Liquid samples are transferred by a syringe equipped with a 4½" needle to discharge the sample below the surface of the vessel solution (see Figure 5). If the analysis is to be based on the volume transferred, care must be taken to remove all air bubbles from the syringe and needle. The volume may be entered when the AQUATEST IV displays mg ; in this case, the result will be obtained on a weight per volume basis. (Note: to obtain the result in weight per weight percent, enter the weight of the sample, found by multiplying the volume of the sample by its density.)

D-15

An alternative method of handling liquid samples is to weigh the syringe before and after transfer. This eliminates the worry about air bubbles. While the titration proceeds, the second weighing can be done and subtracted from the first weight. Then, after the titration is finished (in micrograms) the weight is entered, and the AQUATEST IV will display the result in weight per weight percent.

7.3 Solid Samples

Solid samples can be introduced directly into the titration vessel; weigh the solid in a micro-weighing tube. Remove the support for the sample membrane and dump the sample into the vessel solution taking care to miss the walls. Cover the opening with the Teflon plug. (See Figures 6 and 7.)

It is recommended that after several samples, the titration vessel be thoroughly dried out. Turn off the stirrer; remove the vessel from the clamp and swirl. Replace the vessel and restart the stirrer. Then depress ⎣START⎦ and *WAIT* may appear. Introduce the sample when *SMPL* shows.

When solid samples are introduced, an extraction delay time will be necessary. With materials which dissolve in methanol or pyridine 0.5 minutes may be adequate. With crystalline and other materials which dissolve or disperse gradually, a 5 minute stirring time may be more appropriate. This must be determined with a typical sample.

For this reason, and also for the reason that solids may accumulate in the vessel, an alternative procedure is recommended when analyzing solids and semi-solids. Weigh a quantity of such material and transfer it to a serum bottle containing a measured volume of solvent such as methyl alcohol, dioxane, pyridine, etc. Stopper the bottle and invert a few times over a 30 minute period.

Remove an aliquot right through the serum stopper with a syringe and analyze it as a liquid sample. The water blank of the solvent must be determined separately and entered into the AQUATEST IV. A convenient sample is 1 ml out of a total of 10 ml, and by entering 1/10 of the sample weight the result will be displayed directly in weight per weight percent.

7.4 Inappropriate Samples

If samples containing over 10,000 micrograms of water have been introduced inadvertently, it will take an excessively long time to titrate and the vessel will be contaminated with water. (Note: 1 microliter of water equals 1000 micrograms.) The recovery can be accelerated by carefully adding a quantity of solution B until the display stops counting.

There are also a few materials which react with the reagent so rapidly that they match or exceed the titration rate. This is rare, but it has been found, for example, with cyclohexanone, which therefore cannot be analyzed. The AQUATEST IV keeps on titrating until the entire sample is neutralized. To hasten recovery of the system, add solution E as above.

When large samples of strong oxidizing agents are analyzed, the opposite effect may occur. This will be apparent because the vessel solution darkens due to the liberated iodine. An example of such materials is 50% barium persulfate. The sample cannot be analyzed and the display indicates *WAIT*. To hasten recovery of the system, carefully introduce neutralizing solution until the vessel returns to its amber color.

⎣WARNING⎦

·Strong oxidizing agents should be handled with caution. Do not attempt to analyze organic peroxides.

8. MAINTENANCE AND SERVICE

8.1 Daily

Withdraw excess generator solution using the plastic syringe to which the tubing is attached until the level is approximately 1 cm above the bottom of the generator.

If the instrument has been standing unused for many hours or overnight, or if there is reason to suspect moisture on the inside of the vessel, it may be necessary to dry the vessel. Stop the stirrer and remove the vessel from the clamp. Then, with the electrode connections undisturbed, swirl the vessel just vigorously enough to wash the inside of the vessel. Finally, return the vessel to the clamp and restart the stirrer.

8.2 As Needed

8.2.1 Decanting of Vessel Solution

After a number of samples have been added, the titration vessel will fill up. When the level is approximately 5 cm (2") from the cover, stirring will be inadequate and some solution must be removed. Do this with the plastic syringe. This operation may be repeated once again; however, after that the vessel solution will be overly diluted and must be renewed.

The situation is different if immiscible samples such as oils are analyzed. The latter will form a layer on top of the vessel solution. Approximately 30 ml will be the limit for good mixing of further samples, possibly less with viscous oils. However, if the oil layer is decanted, the vessel solution will not suffer dilution and can be reused for many samples. To decant the oil, turn off the stirrer. After the oil rises to the top, withdraw it using the oil syringe and needle; then restart the stirrer. A titration vessel with a spigot to facilitate decanting is available under Cat. No. 26-122-53.

8.2.2 Replacement of Generator Solution

The role of the generator solution is to act as a catholyte compatible with Karl Fischer reagent. The generator solution as supplied is dark brown due to free iodine. This is an active Karl Fischer reagent which tends to dry out the generator compartment. As the titrations proceed, the free iodine is reduced and the color will lighten. This is perfectly normal. With a light workload, and with the vessel solution seeping in and the reaction products being withdrawn daily, the generator solution will not require frequent replacement. However, with heavy loads, the conductivity of the generator solution will decline, and a point will be reached where the AQUATEST IV will indicate $Error\ So\ In$. Then new generator solution should be introduced after all of the spent solution has been removed using the plastic syringe.

8.2.3 Replacement of Vessel Solution

Stop the stirrer and loosen the three thumb screws of the vessel cover and swing the tabs away from the vessel. Remove the cover assembly and the magnetic stirring bar; then remove the vessel solution. Reassemble the vessel and cover, return the vessel to the clamp on the post, and fill it with a premixed charge of fresh vessel solution. Finally, restart the stirrer and neutralize the new solution as described in Section 6. It is suggested that the generator solution be replaced at this time as well.

The vessel solution has an inherently large titration capacity; however, it may need replacement after several weeks of use. There are two main causes of a decreased lifetime of the vessel solution. One is the parasitic reactions (e.g. ketal formation) which cause drift. A gauge of this is that *the initial and final values differ greatly.* For example, if the initial display is 1000 and the final display is 700 mcg , then fully 30% of the current served to compensate for this "drift". The other cause is that these parasitic reactions themselves use up the reagent as the compensation proceeds continuously day and night. By way of example, if 1 gram of acetone were to be analyzed for water, approximately 300 milligrams of water generated by acetal formation with the reagent must eventually be titrated even though the sample itself may have only contained a few micrograms of water.

In consequence, if carbonyl compounds such as ketones are analyzed, the vessel solution will need more frequent renewal. A good practice is either to wait for the AQUATEST IV to titrate out the background until the uncorrected and corrected values are close, or to change the vessel solution at that time.

Yet another cause of the decay of the vessel solution is the leakage of catholyte. This will manifest itself by the excessive darkening in color of the vessel solution. This effect can be minimized by withdrawing the bulk of the generator solution at the end of the working day, preventing seepage back into the vessel overnight.

8.2.4 Replacement of Membranes

After repeated insertion of the hypodermic needle, the rubber membrane will be visibly torn or open. At this point, unscrew the cap, discard the old membrane and insert a new one in its place. Replace the cap.

8.3 Error Indications

8.3.1 Error So In

This message in the display indicates excessive resistance in the coulometer circuit. The remedy is as follows:

(a) Check that the banana plugs are securely in the corresponding jacks of the post. If secure, inspect the platinum wires to both anode and cathode. If they are intact and there is electrical continuity to the plugs, proceed to b.

(b) Aspirate as much of the generator solution as possible using the plastic syringe with tubing. Discard the solution and pour in the contents of a fresh vial of generator solution. If this does not make the error signal disappear, proceed to c.

(c) Recharge the vessel (see 8.2.3 above). If the error signal still persists, proceed to d.

(d) Clean the frit. The generator is made of Pyrex, platinum and Teflon, and thus will withstand most solvents and strong acids; methanol and concentrated nitric acid are the more commonly used solvents. Use of a vacuum pump to pull solvent through the frit helps ensure that the pores in the frit are clear. A #3 stopper fitted with a glass tube and connected to a vacuum pump by flexible tubing serves the purpose well. First, remove the cover of the vessel and the generator cap; then pour out the generator solution and discard it. Fill a small beaker with enough solvent to cover the frit as the generator is lowered into it. Attach the vacuum and pull enough solvent through the frit to at least cover the cathode. Empty the generator and repeat the procedure twice more or until all deposits are removed. Then pull water through the frit and then methanol. Finally dry the entire assembly in an oven for at least 30 minutes at 65°C. The unit is then reassembled as described in Section 6.

8.3.2 Error ELEC

This message in the display indicates an open circuit in the sensing electrode. First check if the electrode is properly plugged in. If so, inspect the cable for a break. Ultimately, replace the electrode.

> ### WARNING
>
> Karl Fischer reagent is toxic. During handling of the solutions, limit breathing of the vapors and perform all operations in a well-ventilated area. Because Karl Fischer reagent is not biodegradable, Photovolt recommends that it be collected by an industrial waste disposal company (see the Yellow Pages of your telephone directory). The waste should be stored in the interim in a closed glass container.

9. THE METHOD

9.1 Historical

The determination of water is one of the most important and most widely practiced analyses in industry. The field of application is so large that it is the subject of a 3-volume monograph *Aquametry*.[1] Of all the techniques the Karl Fischer titration[2] is the most useful and generally applied. It relies on the specificity to water of the reagent devised by Fischer. The latter contains pyridine, sulfur dioxide, and iodine in an organic solvent. It reacts with water quantitatively:

$$C_5H_5N \cdot I_2 + C_5H_5N \cdot SO_2 + C_5H_5N + H_2O \longrightarrow 2C_5H_5N \cdot HI + C_5H_5N \cdot SO_3$$
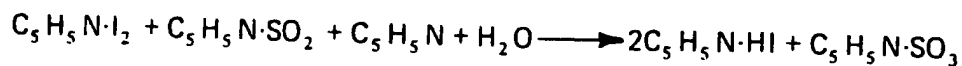
There is a secondary reaction with the methanol (solvent):

$$C_5H_5N \cdot SO_3 + CH_3OH \longrightarrow C_5H_5NH \cdot SO_4CH_3$$
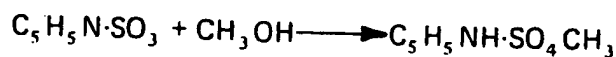
It is noted that although this reaction is specific and quantitative, some difficulty may be caused by any admixed impurities which can react with the solvent to form water, interfere by redox reaction, or which bind iodine or react chemically with the other constituents. Usually these side reactions are much slower than the reaction with water, and although they might be distinguished, such reactions cannot be eliminated. Altogether, the Karl Fischer titration technique is successful in most problems and its use has shown a steady growth over the past 40 years.

Various improvements of the original technique are also of long standing. Karl Fischer himself suggested that an electrometric endpoint detection could be used instead of the visual observation of the disappearance of the dark color of iodine. Almy and Griffin[3] used a potentiometric endpoint successfully. However, an even sharper endpoint detection was introduced by Wernimont and Hopkinson[4] who employed the "dead-stop" method of polarized sensing electrodes.[5] The various commercial instruments are all based on this method, by now considered classic.

However, in 1959, Meyer and Boyd demonstrated the possibility of coulometrically generating iodine in Karl Fischer titrations.[6] This was a novel concept with great potential advantages. If the reagent mix contains iodide together with pyridine, sulfur dioxide and a solvent, the necessary iodine to complete the Karl Fischer reaction can be generated by passing electric current through the titration chamber. When the geometry of the cell and other conditions are properly chosen, 100% current efficiency can be maintained. When this is the case, according to the basic laws of coulometry 96,500 coulombs = 1 chemical equivalent (Faraday number). A Karl Fischer coulometer is then an *absolute* instrument, and the analysis requires no calibration or standardization. The coulometer can be governed by the classic dead-stop electrode. As the latter governs the reaction back to the original set-point, sample after sample can be titrated in the same solution. This system then can be essentially all-electronic, obviating the need for handling liquids, burettes, etc.; this is of particular advantage in this case because the Karl Fischer reagent is noxious and somewhat toxic. Additionally, an electronic system lends itself to automation.

9.2 Photovolt's AQUATEST

These advantages were recognized and a number of coulometric Karl Fischer titrators were employed in research.[7] The first demonstration of such a system in routine analysis was by Shaw and Goode.[8] Encouraged by this background information the first commercial instrument, the AQUATEST,[9] was produced by Photovolt. It had a typical accuracy of 1% and a sensitivity of about 20 micrograms of water. What made it particularly attractive as an industrial quality control instrument was that it read directly in micrograms of water and that the only control was a "Start" switch to initiate the titration.

One vexing problem was keeping the reagent free from deterioration by ambient humidity; thus this model was designed with a completely closed titration vessel. However, whenever positive or negative pressure developed, the liquid was pumped from the cathode to the anode, or vice versa. It was then found that the vessel solution, which lacks iodine, is not nearly as hygroscopic as the usual Karl Fischer reagent. Consequently, a new version, the AQUATEST II, was built with a pressure-equalizing vent. The cathode chamber and configuration was also improved and the instrument exhibited superior performance.[10] The AQUATEST II enjoys widespread use, and a number of papers have been published on its performance in the field.[11] It is also accepted in an official test method.[12]

The AQUATEST IV is a newer version of these instruments. It is the result of a further study[13] in which the limiting factors were scrutinized. Changes include an asymmetric sensing electrode, a cover fastened by a clamp which reduces still further the seepage of ambient humidity, and a stepping motor that provides more reliable performance. Together, these changes tend to reduce electrical noise.

The AQUATEST IV incorporates a microprocessor which offers the advantages pointed out above. The most important is, perhaps, that it serves to distinguish between the titration of water in the sample and water which is slowly generated by parasitic reactions, ambient humidity which seeps in, or any other effects which are oxidizing (or reducing) in character. All these effects, conveniently called "drift", are determined subsequent to the titration proper, and the result of the titration is automatically corrected. The microprocessor also performs the arithmetic operations. There are no controls other than the keyboard, which incorporates all the functions as described in Section 3 above.

The operation is based on the principles of all AQUATESTs. When the instrument is started and a sample is added to the vessel solution, a voltage arises across the polarized sensing electrode which indicates a "wet" condition. This triggers the coulometer and a constant current flow from the anode through the frit, which separates the vessel solution (anolyte) from the generator solution (catholyte), to the cathode. In consequence, iodine is developed at the anode by oxidation of iodide. The iodine completes the Karl Fischer reagent and is mixed by stirring throughout the vessel. When all the water has reacted, the voltage at the sensing electrode drops. This signals the coulometer to stop, and the electrical charge integrated during the titration process is stored in memory. During the subsequent time period of approximately one minute data are taken to establish current requirement, both positive and negative, to maintain the solution at equivalence. These data are then used to correct the initial titration value to reflect the net value due only to the water content of the sample without the background "drift".

The circuit of the AQUATEST IV is shown in Section 10.

9.3 References

1. Mitchell, J. Jr., and Smith, D.M., *Aquametry* John Wiley & Sons, New York, Second Edition 1977

2. Fischer, K., Angew, Chem. *48*, 394 (1935)

3. Almy, E.G., Griffin, W.E., and Wilcox, C.S., Ind. Eng. Chem., Anal. Ed. *12*, 392 (1940)

4. Wernimont, G., and Hopkinson F.J., ibid. *15*, 272 (1943)

5. Foulk, C.W., and Bawden, A.T., J. Am. Chem. Soc. *48*, 2045 (1926)

6. Meyer, A.S. Jr., and Boyd, C.M., Anal. Chem. *31*, 215 (1959)

7. Swensen, R.F., and Keyworth, D.A., ibid *35*, 863 (1963) also Pribyl, M., and Slovak, Z., Mikrochim. Acta, *6*, 109 (1964), Lindbeck, M.R., and Freund, H., Anal. Chem. *37*, 1647 (1965), Rechnitz, G.A., and Srinivasan, K.Z. Anal. Chem. *210*, 9 (1965), Bizot, J., Bull. Soc. Chim. *1967*, Vol 1, 151, Karlsson, R., and Karrman, K.J., Talanta, *18*, 459 (1971)

8. Shaw, R.G., and Goode, J.V., private communication

9. Seltzer, D.M., and Levy, G.B., Am. Lab. *1*, (9), 30 (1969)

10. Levy, G.B., and Seltzer, D.M., Recent Analytical Developments in the Petroleum Industry, Hodges, D.R., Ed. Chapter XV, Applied Science Publishers, Essex England (1974)

11. Johnson, C.R., Power, March 1971 also Gedener, T.J., and Frey, R. Amer. Lab *7* (3) 47, (10) 43 (1975), *8* (7) 41 (1976), Draper, R., Bakers Dig., June 1977, p. 26

12. ANSI/ASTM D1533-77

13. Lindblom, K.A., et al. Paper #260 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February 1978.

NOTES:
1. ALL CMOS SWITCHES SHOWN WITH CONTROL VOLTAGE = LOGIC "ONE".
2. UNLESS OTHERWISE SPECIFIED, ALL RESISTORS ARE 5%, 1/4W
3. J202 KEYED ON PIN 2

PHOTOVOLT CORPORATION
NEW YORK CITY

TITLE
AQUATEST ANALOG BOARD

DWG. NO. 171 2402

D-22

11. PARTS LIST
Those items marked with an asterisk (*) are supplied with the AQUATEST IV 110V 60Hz.

*Sensing Electrode. 04-124-01

*Membranes (20) + Caps (3) 08-122-02

Automatic Syringe, 1 ml 08-122-03

    Syringe alone 26-121-11

*Solution Removing Kit (plastic syringe) 08-122-04

Oil Syringe + Needle, 20 ml 08-122-10

*Generator Cartridge Assembly 11-122-01

*Vessel Cover Assembly. 12-122-02

Dust Cover 21-122-90

*Titration Vessel 26-122-01

*Generator Cap 26-122-11

*Magnetic Stirring Bar 26-122-50

*Sample Syringe, 1 ml 26-122-52

Titration Vessel with Spigot 26-122-53

Vacuum Pump 26-122-54

Automatic Syringe, 5 μl 26-122-55

*Generator Solution (6 vials/pkg) 27-122-01

*Vessel Solution (6 btls, part A + 6 btls, part B) 27-122-02

*Neutralizing Solution 27-122-04

*Sealant (5 oz. jar) 27-122-05

Support for Membranes 36-122-04

*Teflon Plug 36-122-06

*Fuse, 3/8-amp 53-133-75

Fuse, 3/16-amp (for 50Hz instrument) 53-131-87

NOTE: As shipped, the Aquatest IV consists of two main cartons. One carton marked "one of two" contains the basic instrument and accessories. The second carton marked "two of two" contains the reagents, and solutions.

Computer and Printer Interface with Aquatest IV.

RS-232C Port Function Description

Description:
The RS-232C port is accessed upon the occurence of one of the following conditions: The actuation of the MCG key; The actuation of the %PPM, Enter Key Sequence; or the end of the measurement cycle. When this port is accessed, the AQUATEST IV outputs a positive voltage on pin 8 to indicate to the equipment connected to the port that it is ready to transmit data on pin 3. It then polls pin 6 and 20 for a positive voltage. The presence of positive voltage indicates that the equipment is ready to receive data from AQUATEST IV on pin 3. The AQUATEST IV will then serially transmit 7-bit ACII data with no parity, one stop bit, one start bit at 300 baud. Data is transmitted in the following sequence: The control character *RS;* a five digit ID number followed by a space; a two digit serial sample number followed by one space; the sample value followed by a space; and units in either ppm or mcg. The transmission is terminated with a carriage return. The system will remain in this ready-to-print mode until the start key is actuated, indicating the start of a new measurement cycle.

Table 1. RS-232 Connector Definitions

25 Pin D-Connector Pin Number	EIA Interface Pin Description	AQUATEST IV Pin Description
1	Protective Ground	Chassis Ground
2	Transmitted Data	Received Data
3	Received Data	Transmitted Data
6	Data Set Ready	Data Set Ready Detector
7	Signal Ground	Signal Ground
8	Received Line Signal Detector	Received Line Signal
20	Data Terminal Ready	Data Terminal Ready Detector

Table 2. RS-232C Electrical Specifications

NOTATION	Interchange Voltage	
	Negative	Positive
Binary State	1	0
Function	OFF	ON
Voltage Range	−5v to −15v	+5v to +15v

APPENDIX E

Description of Accumet Apparatus
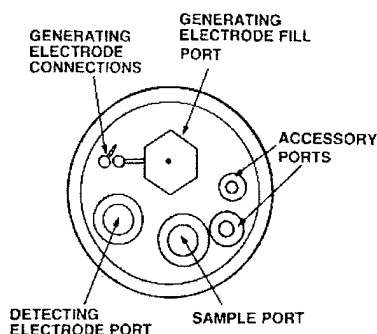
Coulomatic Reaction Vessel

This sealed glass vessel contains a small, inner cathode compartment 1 within a large anode compartment 2 into which the sample is introduced. Reagent solutions in the two respective compartments connect through a glass frit 3. Electrolytic current passes between the platinum wire-mesh anode 4 and cathode 5. Iodine is generated at the anode and reacts immediately with the water in the sample solution. When all the water has reacted, the presence of an excess of iodine is detected by the platinum detecting electrode 6 as a decrease in solution resistance. This terminates the titration, and the quantity of water is calculated automatically as a direct function of the integrated total of electrolytic current consumed.
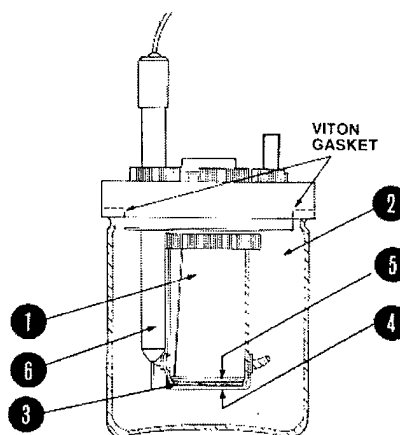
Coulomatic Titrimeter

The Model 447 Coulomatic Titrimeter determines the moisture content of samples by automatic titration with coulometrically generated Karl Fischer reagent. In the Karl Fischer reaction, iodine reacts with water in the presence of sulfur dioxide, an organic nitrogen base, and an alcohol:

$$I_2 + H_2O + SO_2 + ROH + 3RN \rightarrow 2RN\_HI + RN\_HSO_4R$$ **Error! Switch argument not specified.**
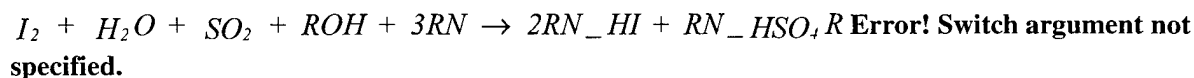
With volumetric titrators, the Karl Fischer reaction is applied to water measurements by means of an iodine-based titrant, with the required sulfur dioxide, alcohol, and nitrogen base present in the titration solvent or the titration against known standards. Thereafter, the titrant volume required to react completely with a sample provides a measure of the sample water anodic oxidation of an iodide contained in the cell reagents. The sample water content is then determined directly by electronically integrating the current required to generate sufficient iodine to precisely react with the sample.

The Coulomatic reaction cell (Figure 1) consists of a sealed vessel with a Teflon cap, housing an iodine-generating electrode and a sensing electrode. The cap assembly provides support for both electrodes, access to fill the generating electrode with solution, and a sample introduction port (with septum). The generating electrode consists of a glass tube with inner (cathode) and outer (anode) platinum screens, separated by a glass frit. Iodine for the Karl Fischer reaction is generated at the anode, while an equivalent amount of a reducing species from reacting with the iodine as it is separated from the anode by means of a glass frit. To prevent bulk liquid flow from carrying the unwanted reducing species through the frit, the liquid level in the reaction vessel is always kept above that in cathode compartment.

The sensing probe is a dual platinum electrode to which a voltage is continuously applied. As in the volumetric method, the endpoint is sensed amperometrically as the sharp decrease in cell resistance that accompanies the trace excess of highly conductive iodine following the elimination of the last sample water.

The Coulomatic combines both speed and accuracy by varying the titration rate in proportion to proximity to the reaction endpoint. When far from the endpoint, generation proceeds at a maximum (nominal) 2.5 mg of water per minute; this rate then is successively diminished to near-zero by the system titrant demand circuitry as the endpoint is approached. Between samples, iodine generation continues "on-demand" to ensure that the endpoint is held and the instrument is always ready for immediate use. Normally, the standby condition is used only to initially set up accessories or the reagent capacity warning, or to stop the stirrer while reagents are changed.

While continuously maintaining the endpoint between samples, the Coulomatic migration of cathode compartment species through the frit, and chemical interferences from prior samples (e.g., reactive carbonvis). This measured drift rate is then used by the Coulomatic to automatically provide correction to subsequent sample analyses.

APPENDIX F

Test Data

TABLE F-1A: RESULTS OF MODIFIED ASTM D 6079 HFRR TESTS IN MM

Humidity	Water, %		Cat 1-H			Jet A-1			Jet A + DCI 4A		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run2	Average
Ambient*	**0**	**0**	**0.240/68**	**0.230/51**	**0.235**	**0.755/65**	**0.730/65**	**0.743**	**0.810/59**	**0.660/54**	**0.735**
No Bulk Water											
0	0	0	0.250	0.235	0.242	0.575	0.620	0.598	0.725	0.645	0.685
10	0	0	0.335	0.330	0.333	0.680	0.540	0.610	0.610	0.720	0.665
50	0	0	0.320	0.335	0.328	0.540	0.505	0.523	0.690	0.525	0.608
100	0	0	0.270	0.355	0.313	0.740	0.565	0.653	0.475	0.555	0.515
Water Added to Reservoir											
100	2	0	0.200	0.210	0.205	0.745	0.725	0.735	0.660	0.730	0.695
100	0	2	0.205	0.240	0.223	0.735	0.730	0.733	0.610	0.820	0.715
Presoak Prior to Test											
0	50	0	0.205	0.245	0.225	0.750	0.725	0.738	0.665	0.640	0.653
0	0	50	0.220	0.275	0.248	0.685	0.755	0.720	0.800	0.655	0.728
Emulsified Prior to Test											
100	0	0	0.190	0.205	0.198	0.720	0.775	0.748	0.740	0.665	0.703
100	5	0	0.285	0.275	0.280	0.600	0.540	0.570	0.465	0.495	0.480
100	10	0	0.300	0.300	0.300	0.505	0.545	0.525	0.620	0.580	0.600
100	0	5	0.300	0.295	0.298	0.590	0.545	0.568	0.625	0.585	0.605
100	0	10	0.250	0.275	0.263	0.775	0.850	0.813	0.630	0.615	0.623

*Wear scar diameter in mm/ambient laboratory humidity

TABLE F-1B: RESULTS OF MODIFIED ASTM D 6079 HFRR TESTS IN MM

Humidity %Rh	Water, % Deionized	Salt	ISOPAR Run 1	Run 2	Average	California DF-2 Run 1	Run 2	Average	Gold Line Run 1	Run2	Average
Ambient*	0	0	0.550/54	0.370/55	0.460	0.490/67	0.440/52	0.465	0.195/67	0.165/65	0.180
No Bulk Water											
0	0	0	0.460	0.510	0.485	0.410	0.415	0.413	0.165	0.350	0.258
10	0	0	0.620	0.500	0.560	0.400	0.435	0.418	0.305	0.160	0.233
50	0	0	0.390	0.485	0.438	0.380	0.430	0.405	0.275	0.310	0.293
100	0	0	0.640	0.585	0.613	0.435	0.345	0.390	0.170	0.295	0.233
Water Added to Reservoir											
100	2	0	0.590	0.570	0.580	0.510	0.515	0.513	0.210	0.195	0.200
100	0	2	0.570	0.510	0.540	0.500	0.500	0.500	0.255	0.240	0.248
Presoak Prior to Test											
0	50	0	0.620	0.610	0.615	0.500	0.505	0.503	0.215	0.190	0.203
0	0	50	0.615	0.580	0.598	0.505	0.495	0.500	0.180	0.175	0.178
Emulsified Prior to Test											
100	0	0	0.645	0.645	0.645	0.510	0.505	0.508	0.170	0.185	0.178
100	5	0	0.495	0.430	0.463	0.445	0.440	0.443	0.260	0.235	0.248
100	10	0	0.475	0.425	0.450	0.440	0.570	0.505	0.170	0.190	0.180
100	0	5	0.600	0.740	0.670	0.530	0.530	0.530	0.195	0.210	0.203
100	0	10	0.750	0.745	0.748	0.655	0.670	0.663	0.180	0.225	0.203

*Wear scar diameter in mm/ambient laboratory humidity

TABLE F-2A: WATER CONTENT DURING HFRR TESTS IN PARTS PER MILLION NEAT FUEL (% OTHERS)

Humidity %Rh	Water, % Deionized	Salt	Cat 1-H Run 1	Cat 1-H Run 2	Cat 1-H Average	Jet A-1 Run 1	Jet A-1 Run 2	Jet A-1 Average	Jet A+ DCI Run 1	Jet A+ DCI Run 2	Jet A+ DCI Average
No Bulk Water											
Ambient											
0	0	0	**170**	**138**	**154**	**127**	**136**	**131**	**89**	**101**	**95**
10	0	0	110	142	126	82	85	83	83	98	90
50	0	0	109	164	136	87	87	87	88	89	88
	0	0	106	166	136	84	85	84	83	120	101
100	0	0	104	168	136	87	82	85	83	124	103
Water Added To Reservoir											
100	2	0	159	159	159	96	96	96	92	86	89
100	0	2	165	153	158	89	83	86	90	113	101
Presoak Prior to Test**											
0	50	0	165/147	159/142	153	100/101	90/111	100	103/104	112/112	108
0	0	50	142/153	141/151	146	93/100	85/95	93	94/120	98/101	103
Emulsified Prior to Test											
100	0	0	N/A	N/A	N/A	116/117	106/120	114	98/102	92/105	99
100*	5	0	3.7/2.4	2.9/1.9	2.72	1.6/1.7	0.8/0.3	1.10	3.2/0.1	4.1/1.9	2.3
100*	10	0	9.0/5.1	6.4/4.5	6.25	1.0/1.6	2.6/0.9	1.52	3.0/3.3	3.0/1.5	2.7
100*	0	5	4.8/2.3	5.1/3.3	3.87	1.7/0.9	1.7/0.1	1.10	2.5/1.8	4.9/0.8	2.5
100*	0	10	7.5/5.0	9.9/6.2	7.15	1.3/1.5	2.1/1.0	1.47	6.9/20.6	10.3/8.1	11.4

*Results in Volume Percent
** Results of Duplicate Determinations

TABLE F-2B: <u>WATER CONTENT DURING HFRR TESTS IN PARTS PER MILLION NEAT FUEL (% OTHERS)</u>

Humidity	Water, %		ISOPAR			California DF-2			Gold Line		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
No Bulk Water											
Ambient											
0	0	0	97	90	93	34	35	34	48	107	77
0	0	0	55	97	76	40	47	43	54	68	61
10	0	0	59	74	66	42	40	41	56	76	66
50	0	0	49	107	78	46	63	54	61	84	72
100	0	0	51	96	73	48	62	55	65	104	84
Water Added To Reservoir											
100	2	0	88	78	83	66	67	66	81	87	84
100	0	2	77	73	75	71	78	74	83	81	82
Presoak Prior to Test											
0	50	0	81/86	77/83	82	73/77	73/74	74	94/85	79/89	87
0	0	50	78/86	70/78	78	79/71	67/71	72	100/87	93/92	93
Emulsified Prior to Test											
100	0	0	102/109	98/106	104	70/74	80/87	78	85/77	93/76	83
100*	5	0	1.6/0.8	1.5/0.2	1.02	2.8/0.7	2.9/1.0	1.85	2.6/1.4	4.0/1.3	2.32
100*	10	0	1.5/0.6	2.4/1.5	1.50	7.8/6.9	11.1/1.6	6.85	2.6/2.9	7.8/3.6	4.22
100*	0	5	1.7/0.6	2.0/2.4	1.67	3.5/1.5	3.4/0.9	2.32	4.8/1.9	4.5/2.3	3.37
100*	0	10	6.4/6.5	6.6/2.5	5.5	8.3/1.6	8.2/5.4	5.87	8.4/5.5	8.1/6.2	7.05

*Results in Volume Percent

TABLE F-3A: CONTACT RESISTANCE DURING MODIFIED ASTM D 6079 HFRR TESTS IN PERCENT

Humidity	Water, %		Cat 1-H			Jet A-1			Jet A + DCI 4A		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
No Bulk Water											
Ambient*	0	0	71	93	82	35	26	30.5	29	37	33
0	0	0	N/A	53	53	39	32	35.5	36	41	38.5
10	0	0	45	61	53	26	41	33.5	32	53	42.5
50	0	0	54	59	57	28	46	37	33	37	35
100	0	0	66	48	57	30	45	37.5	59	41	50
Water Added to Reservoir											
100	2	0	89	91	90	38	29	33.5	23	23	23
100	0	2	91	89	90	33	31	32	24	30	27
0	50	0	92	88	90	44	29	36.5	39	28	33.5
0	0	50	88	79	84	26	38	32	33	28	30.5
Emulsified Prior to Test											
100	0	0	84	82	83	27	24	25.5	24	25	24.5
100	5	0	23	24	23.5	9	9	9	19	20	19.5
100	10	0	26	26	26	9	9	9	26	32	29
100	0	5	25	24	24.5	9	8	8.5	12	10	11
100	0	10	33	32	32.5	9	14	11.5	17	11	14

*Ambient laboratory humidity

F-7

TABLE F-3B: CONTACT RESISTANCE DURING MODIFIED ASTM D 6079 HFRR TESTS IN PERCENT

Humidity	Water, %		ISOPAR			California DF-2			Gold Line		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
No Bulk Water											
Ambient*	0	0	45	52	48.5	24	N/A	24	85	99	92
0	0	0	53	40	46.5	48	58	53	87	85	86
10	0	0	51	37	44	45	33	39	57	100	78.5
50	0	0	55	46	50.5	53	40	46.5	59	70	64.5
100	0	0	39	33	36	21	71	46	87	70	78.5
Water Added to Reservoir											
100	2	0	62	67	64.5	36	35	35.5	99	96	97.5
100	0	2	64	60	62	33	33	33	88	94	91
Presoak Prior to Test											
0	50	0	44	47	45.5	35	36	35.5	96	99	97.5
0	0	50	42	41	41.5	36	33	34.5	99	99	99
Emulsified Prior to Test											
100	0	0	39	37	38	36	31	33.5	99	99	99
100	5	0	9	9	9	23	25	24	70	72	71
100	10	0	8	9	8.5	10	10	10	60	62	61
100	0	5	8	8	8	9	10	9.5	78	71	74.5
100	0	10	8	8	8	28	15	21.5	63	78	70.5

*Ambient Laboratory Humidity

F-8

TABLE F-4A: <u>RESULTS OF MODIFIED ASTM D 5001 BOCLE WEAR TESTS IN MM</u>

Humidity	Water, %		Cat 1-H			Jet A-1			Jet A + DCI 4A		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run2	Average
						No Bulk Water					
0	0	0	0.560	0.560	0.560	0.730	0.750	0.740	0.540	0.570	0.555
10	0	0	**0.560**	**0.570**	**0.565**	**0.790**	**0.790**	**0.790**	**0.580**	**0.590**	**0.585**
50	0	0	0.540	0.550	0.545	0.840	0.860	0.850	0.520	0.540	0.530
100	0	0	0.580	0.560	0.570	0.990	1.040	1.015	0.520	0.510	0.515
						Water Added to Reservoir					
100	2	0	0.58	0.60	0.59	1.00	0.96	0.98	0.50	0.52	0.51
100	0	2	0.57	0.57	0.57	1.06	1.04	1.05	0.50	0.50	0.50
						Presoak Prior to Test					
0	50	0	0.56	0.57	0.565	0.94	0.92	0.91	0.51	0.50	0.505
0	0	50	0.56	0.56	0.56	0.90	0.91	0.905	0.51	0.51	0.51
						Emulsified Prior to Test					
100	0	0	0.55	0.54	0.545	0.77	0.76	0.765	0.57	0.59	0.58
100	5	0	0.58	0.59	0.585	1.36	1.32	1.340	0.63	0.62	0.625
100	10	0	0.55	0.57	0.56	1.09	1.32	1.205	0.61	0.59	0.60
100	0	5	0.59	0.59	0.59	0.61	0.54	0.575	0.77	0.64	0.705
100	0	10	0.58	0.57	0.575	0.57	0.52	0.545	0.69	0.57	0.630

F-9

TABLE F-4B RESULTS OF MODIFIED ASTM D 5001 BOCLE WEAR TESTS IN MM

Humidity %Rh	Water, % Deionized	Water, % Salt	ISOPAR Run 1	ISOPAR Run 2	ISOPAR Average	California DF-2 Run 1	California DF-2 Run 2	California DF-2 Average	Gold Line Run 1	Gold Line Run2	Gold Line Average
						No Bulk Water					
0	0	0	0.870	0.780	0.825	0.780	0.770	0.775	0.500	0.510	0.505
10	**0**	**0**	**0.840**	**0.760**	**0.800**	**0.780**	**0.770**	**0.775**	**0.510**	**0.490**	**0.500**
50	0	0	0.810	0.760	0.785	0.750	0.740	0.745	0.500	0.500	0.500
100	0	0	0.840	0.720	0.780	0.740	0.750	0.745	0.480	0.480	0.480
						Water Added to Reservoir					
100	2	0	0.85	0.79	0.820	0.74	0.72	0.730	0.48	0.51	0.495
100	0	2	0.91	0.78	0.845	0.76	0.73	0.745	0.49	0.19	0.490
						Presoak Prior to Test					
0	50	0	0.89	0.89	0.89	0.75	0.71	0.730	0.49	0.50	0.495
0	0	50	0.89	0.93	0.91	0.74	0.70	0.720	0.50	0.49	0.495
						Emulsified Prior to Test					
100	0	0	0.86	0.82	0.840	0.71	0.71	0.710	0.51	0.50	0.505
100	5	0	1.42	1.36	1.390	1.50	1.35	1.425	0.53	0.52	0.525
100	10	0	1.33	1.57	1.450	1.33	1.31	1.320	0.56	0.56	0.560
100	0	5	0.84	0.67	0.755	0.77	0.71	0.740	0.54	0.52	0.530
100	0	10	0.55*	0.55	0.550	0.55	0.50	0.525	0.53	0.52	0.525

* Use of salt water in this test produced a visible film on the test cylinder. The resulting wear scar, though small, showed evidence of plastic deformation and was irregular.

TABLE F-5A: RESULTS OF MODIFIED ASTM D 6078 SLBOCLE SCUFFING LOAD TESTS IN GRAMS

Humidity	Water, %		Cat 1-H			Jet A-1			Jet A + DCI 4A		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
			No Bulk Water								
0	0	0	5250	5300	5275	1250	1350	1300	1700	1700	1700
10	0	0	5400	5150	5275	1300	1250	1275	1550	1400	1475
50	**0**	**0**	**5150**	**5300**	**5225**	**1200**	**1250**	**1225**	**1700**	**1650**	**1675**
100	0	0	5350	5050	5200	1100	1050	1075	1950	1850	1900
			Water Added to Reservoir								
100	2	0	4300	4350	4325	1150	1150	1150	1950	1800	1875
100	0	2	4050	4350	4200	1300	1200	1250	1950	1550	1750
			Presoak Prior to Test								
0	50%	0	4600	4600	4600	1300	1200	1250	1400	1450	1425
0	0	50	4500	4450	4475	1150	1100	1125	1500	1600	1550
			Emulsified Prior to Test								
100	0	0	4550	4750	4650	1300	1350	1325	1600	1650	1625
100	5	0	4700	4300	4500	1350	1300	1325	1750	1900	1825
100	10	0	4450	4300	4375	1150	1300	1225	1700	2050	1875
100	0	5	5400	5450	5425	1300	1400	1350	1950	2050	2000
100	0	10	4250	4750	4500	1350*	1400	1375	2100	2150	2125

F-11

TABLE F-5B RESULTS OF MODIFIED ASTM D 6078 SLBOCLE SCUFFING LOAD TESTS IN GRAMS

Humidity	Water, %		ISOPAR			California DF-2			Gold Line		
%Rh	Deionized	Salt	Run 1	Run 2	Average	Run 1	Run 2	Average	Run 1	Run 2	Average
No Bulk Water											
0	0	0	1500	1850	1675	1800	1700	1750	5400	3300	4350
10	0	0	1450	1650	1550	1800	1600	1700	3550	3300	3425
50	**0**	**0**	**1550**	**1500**	**1525**	**1550**	**1650**	**1600**	**5300**	**5250**	**5275**
100	0	0	1600	1550	1525	1550	1500	1525	5100	5500	5300
Water Added to Reservoir											
100	2	0	1600	1450	1525	1600	1600	1600	4900	5100	5000
100	0	2	1600	1550	1575	1750	1600	1675	5400	5400	5400
Presoak Prior to Test											
0	50%	0	1300	1500	1400	1400	1350	1375	5000	4900	4950
0	0	50	1500	1450	1475	1350	1400	1375	5000	5000	5000
Emulsified Prior to Test											
100	0	0	1500	1400	1450	1350	1450	1400	5200	3300	4250
100	5	0	1300	1150	1225	1300	1300	1300	5400	5450	5425
100	10	0	900	1250	1075	1250	1200	1225	5550	5500	5525
100	0	5	1400	1450	1475	1500	1350	1425	5450	5450	5450
100	0	10	1450	1400	1425	1400	1450	1425	5700	5650	5675

TABLE F-6A: WATER CONTENT BEFORE/DURING/AFTER BOCLE TESTS IN PERCENT OR PARTS PER MILLION

Humidity %Rh	Water % Deionized	Salt	Cat 1H Run 1 Bef	Dur	After	Run 2 Bef	Dur	After	Avg	Jet A-1 Run 1 Bef	Dur	After	Run 2 Bef	Dur	After	Avg
			No Bulk Water													
0	0	0	144	—	136	145	—	158	146	116	109	74	119	130	108	109
10	0	0	129	—	139	145	—	157	143	119	107	89	137	129	97	113
50	0	0	140	—	157	147	—	173	154	109	124	99	124	127	125	118
100	0	0	163	—	184	150	—	170	167	99	119	104	120	141	126	118
			Water Added to Reservoir													
100	2	0	141	154	155	153	140	141	147	110	93	89	122	110	103	105
100	0	2	132	209	180	136	173	171	150	97	115	123	108	105	106	109
			Presoak Prior to Test													
100	50%	0	129	127	129	139	127	126	130	80	75	71	80	75	83	77
100	0	50	136	130	136	126	124	127	130	76	81	83	81	80	86	81
			Emulsified Prior to Test													
100	0	0	NA	NA	NA	NA	NA	NA	NA	13	28	25	23	18	18	21
100*	5	0	4.63	1.24	2.16	3.39	3.18	4.18	3.13	1.04	1.15	0.01	0.92	1.23	0.21	0.76
100*	10	0	5.54	3.50	5.20	10.67	6.71	5.51	6.19	1.70	3.39	1.34	5.65	1.67	2.12	2.65
100*	0	5	4.49	3.75	0.85	3.18	4.50	3.54	3.39	1.04	1.37	0.40	1.96	1.35	0.15	1.05
100*	0	10	6.75	6.22	6.63	8.80	6.41	6.00	6.80	7.22	2.00	1.39	2.72	2.09	1.37	2.80

* Results in Volume Percent

TABLE F-6B: WATER CONTENT BEFORE/DURING/AFTER BOCLE TESTS IN PERCENT OR PARTS PER MILLION

Humidity	Water, %		Jet A-1 + DCI 4A							ISOPAR						
			Run 1			Run2				Run 1			Run 2			
%Rh	Deionized	Salt	Bef	Dur	After	Bef	Dur	After	Avg	Bef.	Dur.	After	Bef.	Dur.	After	Avg
									No Bulk Water							
0	0	0	96	54	100	102	89	113	84	127	–	142	122	–	140	133
10	0	0	98	87	113	89	86	121	99	117	–	122	101	–	125	116
50	0	0	99	84	129	94	85	109	100	131	–	130	100	–	137	125
100	0	0	108	88	133	89	99	128	108	125	–	110	99	–	141	119
									Water Added to Reservoir	127						
100	2	0	101	96	100	101	100	113	102	116	107	103	139	125	127	120
100	0	2	108	106	107	93	114	97	104	132	117	134	99	97	96	113
									Presoak Prior to Test							
100	50%	0	82	84	89	77	78	89	83	69	74	78	72	77	84	76
100	0	50	80	81	80	88	85	80	82	77	81	82	74	80	74	78
									Emulsified Prior to Test							
100	0	0	108	102	99	101	102	92	101	77	64	81	69	71	74	73
100*	5	0	2.43	1.94	0.34	5.99	1.81	1.99	2.42	1.02	1.30	0.56	1.82	1.08	0.17	0.99
100*	10	0	1.65	2.73	3.02	6.8	7.11	2.21	3.90	8.16	2.35	0.61	3.73	1.84	0.86	2.78
100*	0	5	2.43	2.21	1.15	1.95	2.51	2.07	2.05	2.07	0.68	0.3	2.05	0.97	0.05	1.02
100*	0	10	3.93	2.48	2.44	6.36	4.56	2.29	3.68	7.74	2.32	0.82	2.56	2.52	0.88	2.81

*Results in Volume Percent

F-14

TABLE F-6C: WATER CONTENT BEFORE/DURING/AFTER BOCLE TESTS IN PERCENT OR PARTS PER MILLION

Humidity	Water, %		California DF-2							Gold Line						
			Run 1			Run 2				Run 1			Run 2			
%Rh	Deionized	Salt	Bef.	Dur	After	Bef.	Dur	After	Avg	Bef.	Dur.	After	Bef.	Dur.	After	Avg
			No Bulk Water													
0	0	0	71	–	58	60	53	94	67	82	–	64	61	56	95	72
10	0	0	68	–	51	71	60	105	71	77	–	76	57	56	99	73
50	0	0	69	–	68	65	54	105	72	98	–	76	55	59	101	78
100	0	0	79	–	66	61	57	110	75	122	–	102	61	48	117	90
			Water Added to Reservoir													
100	2	0	69	77	90	64	69	81	90	79	78	83	86	83	85	82
100	0	2	75	73	83	75	70	67	81	85	78	85	78	79	74	80
			Presoak Prior to Test													
100	50%	0	65	64	64	63	64	64	64	90	69	91	83	81	76	82
100	0	50	60	64	65	74	62	58	64	74	77	84	78	82	82	80
			Emulsified Prior to Test													
100	0	0	39	30	31	47	60	43	42	97	87	91	81	65	63	81
100*	5	0	1.79	0.75	0.07	2.93	0.92	0.01	1.08	3.81	2.64	1.26	4.21	3.83	1.48	2.87
100*	10	0	4.35	1.40	0.91	8.68	4.39	1.02	3.46	7.07	5.34	4.89	6.85	7.17	4.70	6.00
100*	0	5	5.21	0.52	0.24	13.97	4.60	0.96	4.25	5.01	3.11	1.51	5.17	4.50	1.34	3.44
100*	0	10	2.64	1.14	0.09	5.13	4.25	0.95	2.37	5.55	6.42	2.94	7.44	4.91	3.02	5.05

*Results in Volume Percent

TABLE F-7: Affect of Aeration at Various Humidities Using the BOCLE on Moisture Content of Dried Reference #2 Fuel (measurements made using Accumet)

Time Hours	Water Content, PPM		
	0% Humidity	10% Humidity	100% Humidity
Undried Fuel*	103.3	-	-
0**	39.1	43.4	42.8
0.5	39.5	41.3	43.6
1.0	40.7	44.8	47.2
24	45.9	46.6	55.9
49	37.3	60.9	53.9

*Test fuel from the storage container immediately prior to drying
** Dried fuel directly from container immediately prior to transferal to reservoir

TABLE F-8: Affect of Aeration at Various Humidities Using the BOCLE on Moisture Content of Jet A-1 Fuel (measurements made using Accumet)

Time Hours	Water Content, PPM		
	0% Humidity	10% Humidity	100% Humidity
New Fuel*	64	-	-
0**	54.7	56.5	55.6
0.5	57.1	57.3	N/A***
1.0	41.2	59.4	56.3
24	N/A***	61.9	65.9
49	40.01	66.3	83.5

* Test fuel from the storage container prior to drying
** Dried fuel directly from container immediately prior to transferal to reservoir
*** No result is available due to equipment failure

TABLE F-9: Results of Laboratory Wear Tests Following 48 Hours of Aeration

		Dried Reference No. 2 Diesel			Jet A-1		
	Humidity	Baseline*	0.5 Hrs	48 Hrs	Baseline*	0.5 Hrs	48 Hrs
MODIFIED ASTM D 5001	0	0.560	0.640	0.620	0.740	0.650	0.620
(mm)	10	0.565	0.670	0.620	0.790	0.660	0.670
	100	0.570	0.640	0.620	1.015	0.700	0.710
MODIFIED ASTM D 6078	0	5275	5800	5900	1300	1200	1400
(grams)	10	5275	4900	4900	1275	1350	1350
	100	5200	4850	5500	1075	1250	1200
MODIFIED ASTM D 6079	0	–	0.285	0.315	0.597	0.250**	0.625
(mm)	10	0.332	0.315	0.310	0.610	0.180	0.690
	100	0.312	0.220	0.335	0.652	0.730	0.745

* Result obtained with fuel that was not pretreated to remove dissolved moisture
** HFRR result of 0.25 was repeated at the same conditions with a new fuel sample to give 0.550 mm